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Nanotechnology

Methods of treatment and functionalization of carbon nanotubes

Metody úpravy a funkcionalizace uhlíkatých nanotrubiček

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Diploma Thesis Assignment

Student: **Bc. Ondřej Dutko**

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Title: Metody úpravy a functionalizace uhlíkatých nanotrubiček
Methods of treatment and functionalization of carbon nanotubes

Description:
The aim of diploma thesis is to study methods of modification and characterization of carbon nanotubes to compare individual methods and consequently application of achieved results will be used for compilation of methodological procedures the most convenient for demanded applications.

Proposal of diploma thesis content:
1. Introduction and goal of the diploma thesis.
2. Theoretical part.
2.1. Carbon nanotubes, methods of characterization and evaluation of properties.
2.2. Importance of treatment and functionalization of carbon nanotubes.
2.3. Methods of cleaning and treatment of carbon nanotubes.
3. Practical part.
3.1. Treatment and functionalization of carbon nanotubes using selected methods.
3.2. Characterization of treated products.
3.3. Discussion and proposition of methodological procedures.
4. Conclusion.

References:
1. LIKODIMOS, Vlassis, Theodore a. STERIOTIS, Sergios K. PAPAGEORGIOU, George Em. ROMANOS, Rita R.N. MARQUES, Raquel P. ROCHA, Joaquim L. FARIA, Manuel F.R. PEREIRA, José L. FIGUEIREDO, Adrián M.T. SILVA and Polycarpos FALARAS. Controlled surface functionalization of multiwall carbon nanotubes by HNO_3 hydrothermal oxidation. Carbon [online]. 2014, Vol. 69, pp. 311–326. ISSN 00086223.
2. ERNST, Friederike, Timm HEEK, Antonio SETARO, Rainer HAAG and Stephanie REICH. Functional Surfactants for Carbon Nanotubes: Effects of Design. The Journal of Physical Chemistry C [online]. 2013, Vol. 117, no. 2, pp. 1157–1162. ISSN 1932-7447.
3. ANGELIKOPOULOS, Panagiotis and Henry BOCK. The science of dispersing carbon nanotubes with surfactants. Physical chemistry chemical physics : PCCP [online]. 2012, Vol. 14, no. 27, pp. 9546–57. ISSN 1463-9084.
4. SOULIÉ-ZIAKOVIC, Corinne, Renaud NICOLAŸ, Alexandre PREVOTEAU and Ludwik LEIBLER. Dispersible carbon nanotubes. Chemistry (Weinheim an der Bergstrasse, Germany) [online]. 2014, Vol. 20, no. 5, pp. 1210–7. ISSN 1521-3765.
5. ROCHA, Raquel P., Adrián M.T. SILVA, Saudi M.M. ROMERO, Manuel F.R. PEREIRA and José L. FIGUEIREDO. The role of O- and S-containing surface groups on carbon nanotubes for the elimination of organic pollutants by catalytic wet air oxidation. Applied Catalysis B: Environmental [online]. 2014, Vol. 147, pp. 314–321. ISSN 09263373.

Extent and terms of a thesis are specified in directions for its elaboration that are opened to the public on the web sites of the Nanotechnology Centre.

Supervisor: **doc. Ing. Daniela Plachá, Ph.D.**

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Abstract

This work is aimed on studying alterations induced by oxidative functionalization treatments of commercially available carbon nanotubes Nanocyl NC7000 using oxidative agents and resistance to these treatments; aiming to further tune their physicochemical properties and dispersibility. Nitric acid, potassium permanganate, hydrogen peroxide, sulfuric acid and sodium hypochlorite are chosen as representatives of commonly used oxidizers. Their efficiency is studied in different conditions, concretely concentration and temperature, by well-established analytical methods (SEM, FTIR and Raman spectroscopy). Additional carbon phase analysis is employed to obtain more detailed information of samples, as this little used method is capable to replace commonly used TGA. The interpretation of acquired results contains the level of oxidation, functional groups present and metallic impurities removal. Suggestions for selecting specific treatments to fulfill one's demands about final product are also included.

Keywords: carbon nanotubes, oxidation, FTIR, Raman spectroscopy, electron microscopy, carbon phase, functionalization

Anotace

Tato práce je zaměřena na studium změn vyvolaných oxidativními funkcionalizačními postupy komerčně dostupných uhlíkatých nanotrubiček Nanocyl NC7000 s využitím oxidačních činidel a odolnost vůči těmto úpravám; s cílem vylepšit jejich fyzikálně-chemické vlastnosti a dispergovatelnost. Kyselina dusičná, manganistan draselný, peroxid vodíku, kyselina sírová a chlornan sodný jsou zvoleny jako zástupci běžně používaných oxidačních činidel. Jejich účinnost je studována v různých podmínkách, konkrétně koncentrace a teploty, pomocí dobře zavedených analytických metod (SEM, FTIR a Ramanovy spektroskopie). Dále je využita analýza fázového uhlíku k získání podrobnějších informací o vzorcích, jelikož je tato málo používaná metoda schopna nahradit běžně používané TGA. Interpretace získaných výsledků zahrnuje úrovně oxidace, přítomných funkčních skupin a odstranění kovových nečistot. Návrhy na výběr konkrétních postupů pro splnění požadavků na případný konečný produkt jsou také zahrnuty.

Klíčová slova: uhlíkaté nanotrubičky, oxidace, FTIR, Ramanova spektroskopie, elektronová mikroskopie, fázový uhlík, funkcionalizace

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Contents

List of abbreviations

ATR	Attenuated total reflectance
BET	Brunauer, Emmett, Teller - type of isotherm
CNS(s)	Carbon nanostructure(s)
CNT(s)	Carbon nanotube(s)
CVD	Chemical vapor deposition
DFTB	Density functional tight binding - type of computational method
DWCNT(s)	Double-walled carbon nanotube(s)
eV	Electron volt
FTIR	Fourier transform infrared spectroscopy
HRTEM	High resolution transmission electron microscopy
MWCNT(s)	Multi-walled carbon nanotube(s)
NC7000	Nanocyl 7000
Nd:YAG	Neodymium-doped yttrium aluminum garnet
RBM	Radial breathing mode
SEM	Scanning electron microscopy
SWCNT(s)	Single-walled carbon nanotube(s)
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

1 Introduction

In recent years, many studies have been performed in the field of CNTs, as this material represents new generation of nanomaterials with revolutionary properties. Carbon nanotubes are well known for their high length/diameter ratio, thermal stability and conductivity, high specific surface area and electronic properties. However, there are many applications requiring sufficient dispersibility for further development. Right at this point, pristine CNTs are failing, thus requiring additional treatments known in general as functionalization. Covalent and non-covalent functionalizations were performed and their effectiveness studied in terms of structural changes, surfactant adsorption and even biomolecular wrapping.

This thesis is focused on oxidative functionalization treatments of commercially available carbon nanotubes Nanocyl NC7000. For the experimental part nitric acid, potassium permanganate, hydrogen peroxide, sulfuric acid and sodium hypochlorite at various temperatures, concentrations and mixtures will be used. Their efficiency will be analyzed by well-established analytical methods (SEM, FTIR and Raman spectroscopy) and additional carbon phase analysis, replacing commonly used TGA. The results will be interpreted in terms of the level of oxidation, presence of functional groups and metallic impurities removal. Suggestions for selecting specific treatments to fulfill one's demands about final product will be also included.

2 Theoretical part

This part of thesis is focused on the description of carbon nanotubes types and their structure, methods of production, analytical methods for CNTs characterization, methods for their purification, modification and the motivation to perform these modifications. The purpose of this chapter is to bring insight into CNTs structure.

2.1 Carbon nanotubes, methods of characterization and evaluation of properties

Carbon nanotubes are one of the new promising materials in the nanotechnology field. It is almost 25 years since the first scientific study has been released, describing nanotubes as we know them today [1]. Since then, the advance of our knowledge of this material has increased a lot. They exhibit unique structural, chemical and electrical properties. The field of applications for this material is very wide, from pollution adsorbents to nanoelectronics. In the future, the incorporation of CNTs to much more applications can be expected. By the type of application, pristine or modified CNTs are used [2].

2.1.1 Carbon nanotubes structure

Carbon nanotubes can be described as carbon coaxial tubes (walls) with honeycomb structure, very similar to graphene with high length/diameter ratio. Tips of CNTs are usually enclosed with fullerene-like hemispheres. As stated above, we can divide CNTs into 3 groups by the number of walls:

- Single-walled CNTs (SWCNTs)
- Multi-walled CNTs (MWCNTs)
- Double-walled CNTs (DWCNTs)

SWCNTs consist of only single carbon layer. This makes them relatively the most reactive form. They are mostly used in applications, that require well-defined structure (nanoelectronics, optics, etc.). Modifications and defects in the structure increase fragility. Chirality of SWCNTs has major impact on their properties [3, 4].

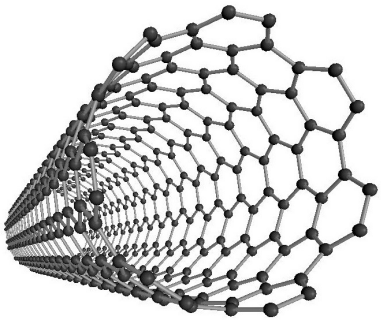

Fig. 1: Model of SWCNTs [4]

MWCNTs are structures with multiple coaxial walls. Their topmost layer has the same reactivity as in SWCNTs, but also serves as cover for inner layers, making them inert until the top layer becomes sufficiently disrupted. MWCNTs are most commonly produced material for industrial applications. As every layer can have different chirality, their usability is lower compared to CNTs. They are used in applications utilizing their surface properties independent on chirality (sorbents development, backbones of tailored molecules, composite materials,…) [4, 5].

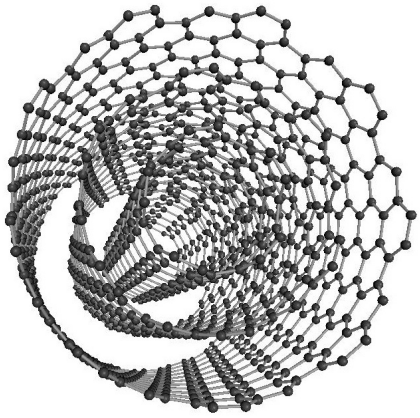

Fig. 2: Model of MWCNTs [4]

DWCNTs are sorted out as a transition between SWCNTs and MWCNTs. Their chiral description is more relevant due to low amount of walls. Nevertheless, some inertia is preserved. Even after the outer layer is damaged, stiffness is also preserved. Due to the presence of properties present in groups mentioned previously, they are used in special applications [4, 6].

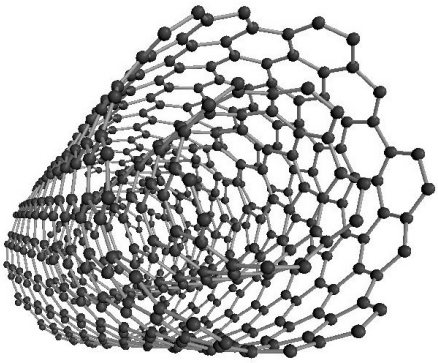

Fig. 3: Model of DWCNTs [4]

Based on the orientation of the tube axis with respect to the hexagonal lattice, the structure of a nanotube can be completely specified through its chiral vector. This generating vector is called Hamada-vector or folding vector (n, m) [7] and has direct impact on CNTs geometry (Fig. 4).

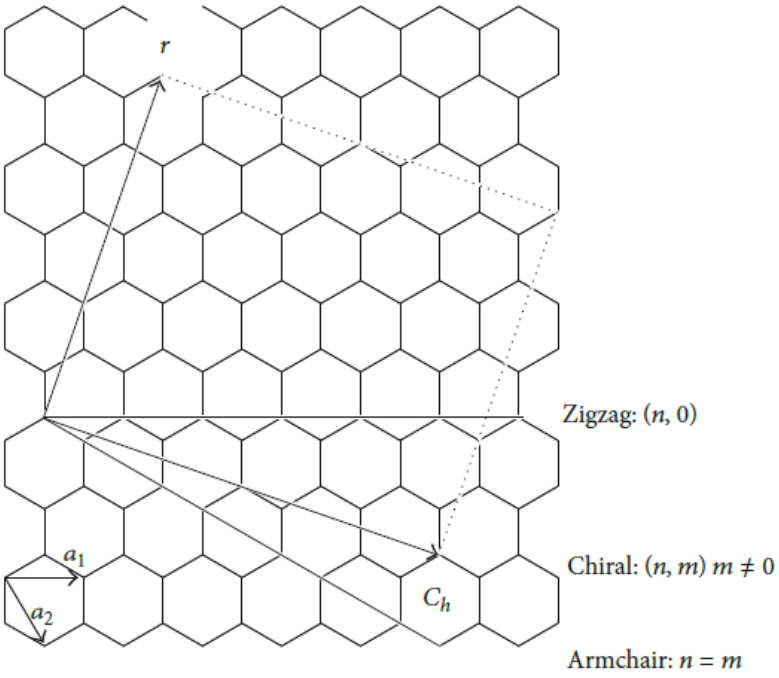

Fig. 4: Description of CNTs geometry. Lattice vectors are denoted as a_1 and a_2 and C_h represents folding vector. Vectors for zigzag and armchair folding are also boundaries of folding possibilities [8]

According to this geometry, we can divide them into 3 groups based on chirality (Fig. 5):

- Zigzag CNTs (n,0)
- Armchair CNTs (n=m)
- Chiral (m≠0,n≠m)

Chirality is very crucial for the CNTs description, especially for SWCNTs. It has direct effect on electronic structure, thus making CNTs having semiconductive or metallic character. CNT is metallic if |n-m| is a multiple of 3, otherwise it is semiconducting with value of band gap inversely dependent on tube diameter; ranging from 1,8 eV (small diameters) to 0,18 eV (for the widest possible stable tube) [8–10]. By further investigations, it has been revealed, that armchair nanotubes are truly metallic, as they have 2 bands crossing at Fermi level. For other metallic configurations, the metallicity is thermally generated, as these structures have band gap in order of ~10 meV [11].

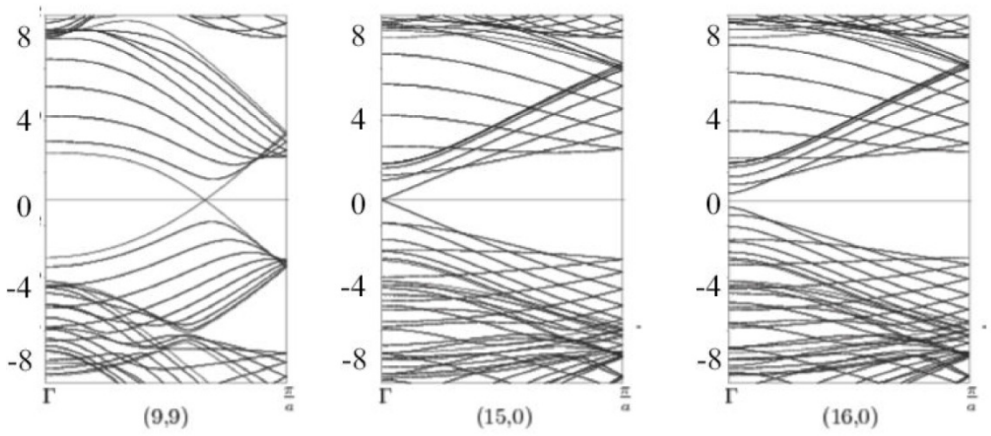

Fig. 5: Band structures for SWCNTs with different (n,m) translation vectors [11]

With recent integration of computation technologies, many properties of CNTs can be calculated using ab-initio methods [12, 13], MD (molecular dynamics) methods or other semi-empirical methods (DFTB – density functional tight binding) and many others [14].

2.1.2 Methods of CNTs synthesis

Various techniques have been developed to synthesize CNTs; most common used are arc-discharge, laser ablation and chemical vapor deposition (CVD). These methods share the same principle; using energy for fragmentation of carbon source (into groups or single atoms). These fragments then recombine to CNTs structure. The main difference among these methods is the form of delivered energy; arc discharge uses electricity, laser ablation uses high intensities of light (commonly laser source) and CVD uses heat [8, 15–18].

Since the discovery of CNTs, arc discharge method is so far the most efficient method in terms of producing high quality material with low amount of structural defects, due to high temperatures generated during the synthesis. However, this method produces CNTs with various chirality, diameters and length. Another downside to this method is high manufacturing cost. Recently, some advances in growth control have been achieved using different buffer gases, specialized catalysts, by applying magnetic field etc. [8, 18].

Laser ablation is the method using high energy lasers to deliver sufficient energy to vaporize carbon instead of electricity used in arc-discharge method. This method also uses graphite as a carbon source, usually mixed with catalyst nanoparticles (Ni or Co) for preferential growth of SWCNTs. Mostly CO_2 and Nd:YAG lasers are used. New advancement might come from using UV laser instead infrared, as excitation energies are higher, thus changing from photothermal to photochemical ablation. Downside to this method is also high cost, as for arc-discharge [8, 18].

Both previously methods are recently used mainly for preparation of SWCNTs, as the production cost would not be justifiable for MWCNTs production, especially of industrial grade material.

Chemical vapor deposition is a method providing nowadays solution to produce CNTs for industrial applications; especially MWCNTs. Compared to previous methods, this one requires lower temperatures (generally about 800 °C) and is well-known for its easily reaction controllability, scalability and tunability. This method is using a non-source substrate (Si, SiO_2, Al, Ni, graphite,…) and carbon source is often delivered into reaction chamber as a gas, most often hydrocarbons. Experiments using alcohols were also reported, improving purity of final product. It is suggested, that oxygen present in alcohols serves as an etching agent, removing amorphous carbon from CNTs during growth [19, 20].

One important thing for all 3 methods is a required presence of catalysts for CNTs growth, especially SWCNTs. It has been demonstrated, that MWCNTs can be grown without catalysts, but SWCNTs cannot. This implies the need to develop catalysts for CNTs specific growth. In the beginning Fe, Ni, Co were used (3d valence transition metals) in CVD. It is assumed, that these catalyst nanoparticles serve as carbon source decomposers and allow restructuralization of carbon atoms to form CNTs [8, 18, 19].

2.1.3 Methods of CNTs characterization and evaluation of their properties

After successful preparation of CNTs, it is most desirable to characterize the final product. Unfortunately, there is no universal all describing method, however many methods available today can yield great deal of information required, ranging from structural to compositional. There are many methods used nowadays, yet only the most used are described below.

2.1.3.1 Morphology/structural analyzing methods

It can be said, that the most popular methods for morphological analysis are scanning electron microscopy (SEM) and transmission electron microscopy (TEM). These two methods are using electrons instead of photons (in optical microscopes); providing grayscale images. SEM is used to obtain images of CNTs bundles to assess shape of nanotubes. Most of the time the images obtained are showing us entangled "spaghetti-like" ropes bundled together [4]. TEM on the other hand allows one to look closer and through individual nanotubes. It is often used to obtain more precise morphology, as the number of nanotube walls, their diameter and defects present. Presence of amorphous carbon can be assumed as well [21, 22]. TEM can be also used to obtain crystallographic information, but sample preparation is extremely difficult and high level of experience is more than demanded for the operator of TEM. It is more suitable to use XRD (mentioned below).

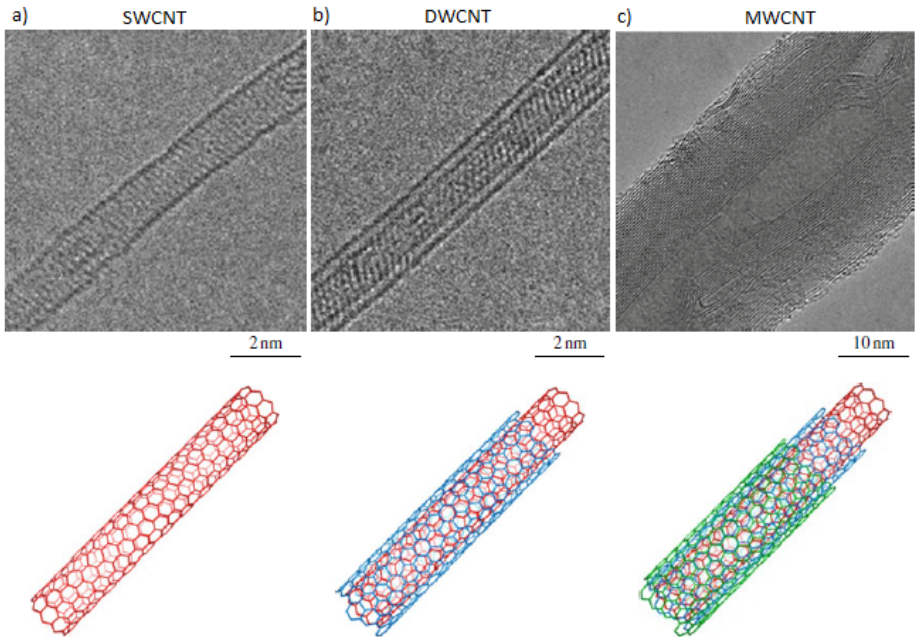

Fig. 6: HRTEM images of a) SWCNTs, b) DWCNTs, c) MWCNTs [23]

As a side-effect, interaction of electrons with sample generates specific X-ray radiation containing information about elemental composition of the sample, thus instrumentation of SEM and TEM often involves X-Ray detectors used for local elemental analysis. By the type of the detector, we can distinguish WDS/EDS (wavelength/energy dispersion analysis).

X-ray diffraction analysis (XRD) is another method used to analyze crystalline structure of the sample. Although nanotubes are not exactly crystal-like, this method can analyze interlayer spacing between walls (002 basal reflections) and give us information about interlayer space distribution [4].

Raman spectroscopy is a method generally used to analyze chemical composition. This method is also sensitive to carbon in sp^2 and sp^3 hybridization. As CNTs with no defects consist of sp^2 carbon (G band) atoms, sp^3 carbon (D band) is present as an impurity (amorphous carbon, defects). Thus Raman spectroscopy provides simple and powerful method as obtained information of chemical composition is directly linked with structure [4, 22, 24]. Examples of Raman spectra are in Fig 7.

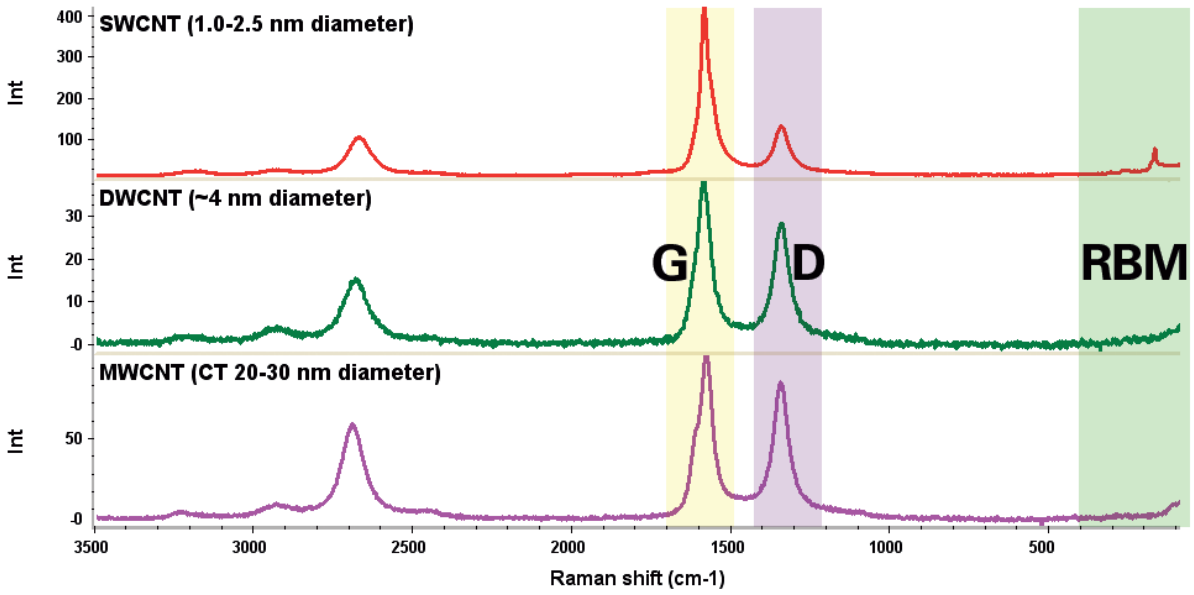

Fig. 7: Examples of Raman spectra of CNTs; with G,D and RBM bands illustrated [25]

In case of SWCNTs, Raman spectroscopy can be used to estimate nanotube diameter from RBM (radial breathing mode) peak position ($d_t = \frac{248}{\omega_{RBM}}$ nm), as ω_{RBM} is dependent on laser excitation wavelength [24].

2.1.3.2 Morphology/structural analyzing methods

Infra-red spectroscopy (IR) is well known complementary method to Raman spectroscopy. It is used to analyze functional groups present in the sample. Although ATR method is very simple in terms of sample preparation, it cannot be used for CNTs, thus KBr pellet method needs to be used. This method is often used to analyze presence of oxygen (-OH, -COOH, =O) groups in CNTs sample [22, 26]. Transmittance spectra are used for qualitative analysis, but when recalculated to absorbance spectra, quantitative analysis can be performed, as absorbance is concentration dependent.

TGA (thermogravimetric analysis) is a thermal analysis method measuring weight loss dependence on temperature. Additional method implemented is DTA (differential thermal analysis) measuring thermal coloring of the sample, thus giving information about possible chemical reactions taking place. Analysis can be performed in inert or oxidative atmosphere [22, 26, 27].

Carbon phase analysis is very similar to TGA. Its principle is to heat sample in flowing oxygen or nitrogen atmosphere with increasing temperature and simultaneously analyzing concentrations of carbon dioxide (CO_2) and water, which are recalculated to carbon and hydrogen concentrations. By the concentration dependence on temperature, we can assume the origin of carbon and hydrogen. The weight of residuals needs to be measured separately. When performed in nitrogen atmosphere, amount of oxygen can be analyzed. It is recommended (especially for CNTs samples) to perform analysis in both atmospheres. TGA and carbon phase analysis can be both used to analyze thermal stability of CNTs as well.

XPS (X-ray photoelectron spectroscopy) is a method capable of elemental analysis. As the energies used are in the same range as energies of chemical bonds, it is possible to analyze them as well. This method is highly efficient for CNTs analysis, as each functional group can be measured, making it efficient to analyze levels of oxidation [27, 28].

2.2 Importance of treatment and functionalization of carbon nanotubes

CNTs are well known for their hydrophobicity [29], making their availability for number of applications limited [30]. Preparation of nanocomposites requires high solubility, electronic applications well-defined structure, drug-delivery systems biocompatibility, etc. Most of the time, CNTs are also demanded separated (not in their bulk form). As written before, CNTs produced also contain impurities (amorphous carbon, catalyst residues,…) or unwanted functional groups. Modification/functionalization is used to make CNTs more suitable for those applications mentioned above or serve as one of the steps for their separation (length, diameter, chirality,…) [31, 32].

2.3 Methods of purification and treatment of carbon nanotubes

Purification treatments are performed to remove impurities and functional groups from the structure [15, 33], while modification treatments are performed to introduce new functional groups and/or new compounds into/onto CNTs structure [35]. There is no distinct difference for these 2 goals in terms of treatments selection, as some of them are used in both categories, thus I will be describing them not by the intended result, but the way they are interacting with CNTs. There are basically 2 ways of interaction: covalent (changing chemical bonds) and non-covalent (preserving existing bonds) [34].

2.3.1 Covalent purification treatments

Methods altering chemical composition of CNTs can be both chemical and physical. The advantage of these methods is progressive way to remove impurities, however at the cost of damaging graphitic structure. There are 2 most common ways to perform this treatment depending on the selected environment: gas phase and liquid phase oxidation.

During gas phase oxidative treatments, carbonaceous impurities are removed at a temperature ranging from 225 °C to 760 °C depending on the atmosphere. The commonly used oxidants include air, O_2, a mixture of Cl_2, H_2O and HCl, a mixture of Ar, O_2 and H_2O, etc. It is advised to maintain even exposure of the material to oxidative atmosphere and select appropriate oxidizing agent for used sample to exploit reaction specificity. For example, high temperature air oxidation of MWCNTs prepared via arc-discharge method is very efficient, as these MWCNTs don't contain metallic impurities. In case of SWCNTs, this way of treatment often leads to destruction of the sample due to the metallic impurities inducing lower temperature oxidation of carbon. Also bundling of CNTs causes uneven exposure. In conclusion, gas phase oxidation is suitable for removing amorphous carbon and opening caps at the ends of CNTs, but insufficient at removing metal impurities [36, 37].

Liquid phase treatments are known for their ability to remove amorphous carbon and metal impurities as well. Principle of these methods is exploiting different reactivity of impurities (higher) compared to sp^2 carbon (lower) in CNTs. Depending on oxidizer selection, certain efficiency level is reached. The commonly used oxidants for liquid phase oxidation include HNO_3, H_2SO_4, H_2O_2 and it is possible to use other well-known oxidizers. Generally, to choose appropriate oxidizer(s), one needs to follow principles of organic chemistry, as CNTs can be viewed as a polyaromatic compound with vast number of aromatic circles [38–40].

HNO_3 is the most commonly used reagent for SWCNT and MWCNTs purification for its mild oxidation ability, which can selectively remove amorphous carbon. It is also inexpensive and nontoxic, capable of removing metal catalysts and no secondary impurities are introduced. Efficiency of HNO_3 is concentration dependent and can be also enhanced in mixtures with H_2SO_4 (used for nitration), but at the cost of introducing more defects into CNTs [38–43].

H_2O_2 is another mild oxidant capable of removing carbon impurities. Big advantage of this oxidizer is its green character, as only water is produced as a waste. However, the disadvantage is its incapability to remove metals. Therefore, it is mostly used in the mixture with HCl. This acid is most favored, because it has no oxidation effect on CNTs and is still efficient to form soluble salts with metal catalysts [37, 44, 45]. Therefore, precipitation of iron and iron hydroxide is hindered. Mechanism is demonstrated below (Fig. 7).

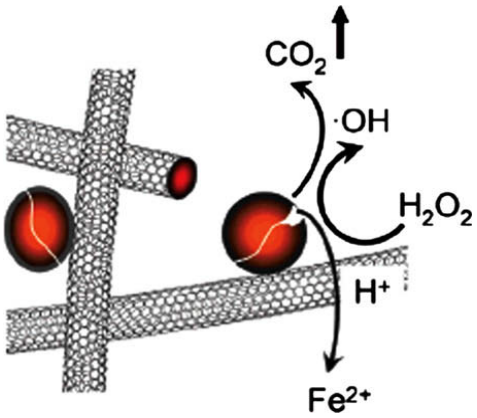

Fig. 8: Mechanism of H_2O_2 disrupting carbon-coated nanoparticles (not in scale) [37]

Another approach is microwave-assisted purification based on high microwave absorption of inorganic acids as HCl, HNO_3 and H_2SO_4, thus enabling rapid metal dissolution without severe damage to CNTs in short time [37, 46].

All these liquid phase treatments can be further enhanced by sonication to further assist dispersion in solutions [47, 48].

2.3.2 Non-covalent purification treatments

Compared to covalent treatments, these are exploiting differences in physical properties between CNTs and impurities, for example aspect ratio, physical size, solubility, etc. There are several methods based on these differences to provide separation, for example filtration, chromatography, centrifugation, high temperature annealing and many more. Some of these methods are performed in solutions, so high dispersibility is required [31, 49–51].

Filtration is a separation method based on the differences in physical size, aspect ratio, and solubility. Small size particles or soluble objects in solution can be filtered out and CNTs with large aspect ratio will remain. Polyaromatic compounds and fullerenes are soluble in CS_2, toluene, etc. This makes filtration useful only to remove easily soluble compounds and particles detached from CNTs. Sonication is also implemented to prevent clogging of the filter and slowing down the whole process [52, 53].

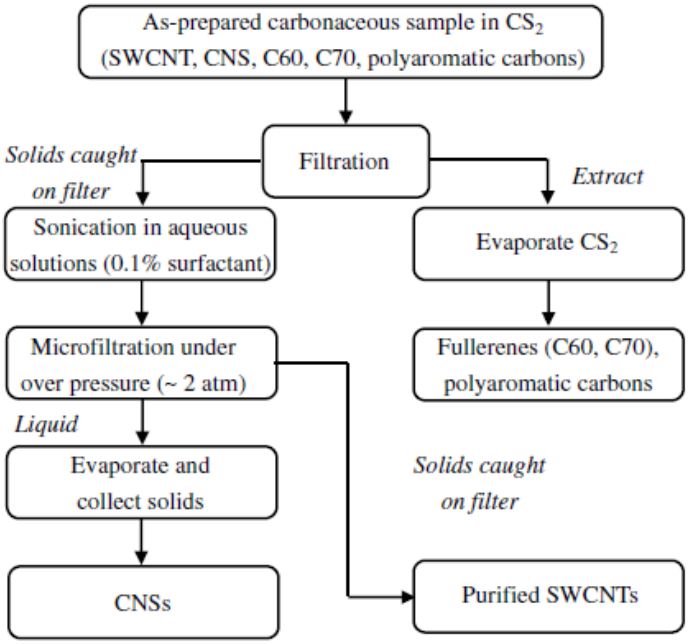

Fig. 9: A diagram of methodology to purify SWCNTs produced with laser ablation [37]

High temperature annealing is a method utilizing high thermal stability of graphite (even at 3000 °C), while boiling points of metals lie in lower temperatures. If proceeded in inert atmosphere (Ar) or vacuum, metal impurities are evaporated, while CNTs structure remains technically "intact". If functional groups are present in CNTs structures, high temperature annealing will remove them as well [54–56]. In brief, this method is one of the most effective to remove metal impurities from accessible zones (tips, hollow core), it also improves crystalline structure (rearranging of carbon atoms), thus improving thermal and electronic properties. If these rearrangements are taking place, we are talking about graphitization (Fig. 10) [57].

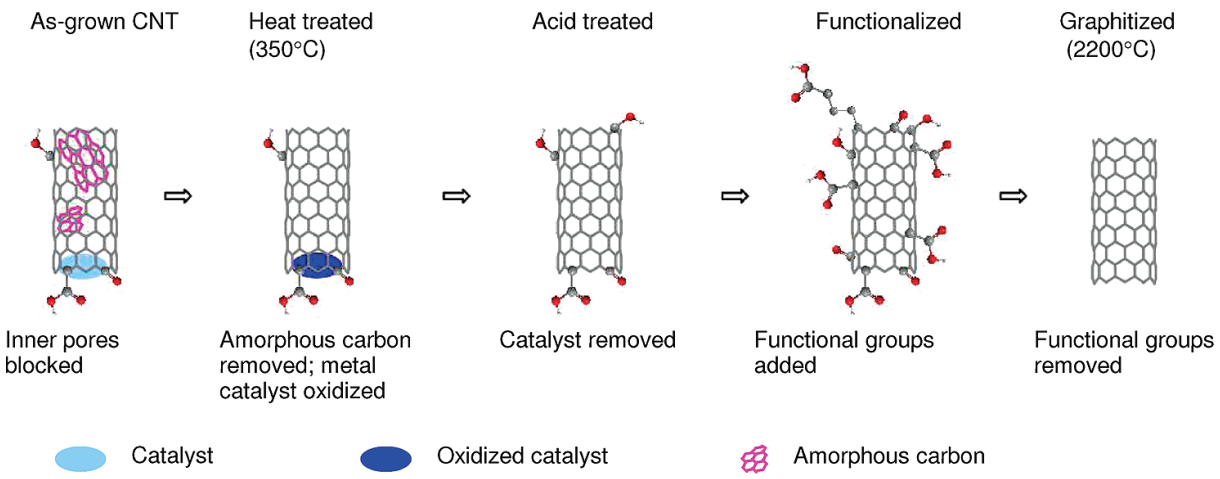

Fig. 10: General scheme of CNTs purification and graphitization [57]

2.3.3 Covalent functionalization treatments

Covalent functionalization strategies are various, from simple oxidative treatments to highly complex additive reactions. Efficiency of functionalization is highly dependent on agents selected as CNTs structure. Caps, open edges and defects in nanotube structure are more reactive compared to undamaged nanotube wall.

Strategies can be divided into 3 groups:

- Introduction of defects and subsequent functionalization (and derivatization)
- Oxidizing ends of nanotubes
- Covalent sidewall functionalization

The most used type of functionalization is oxidation. Methods used are similar to those used for purification (Chap. 2.3.1) except the oxidation is demanded. This can be achieved by using higher temperature, higher concentration of oxidizing agent and longer exposure time. Selection of oxidizers is not limited to those previously mentioned (HNO_3, H_2SO_4, H_2O_2), other agents such as $KMnO_4$, NaOCl, $K_2Cr_2O_7$ can also be used solely or in mixture [2, 5, 15, 42, 58–61].

It is presumed that oxidation is taking place at the ends of nanotubes and defective sites; but in high concentrations, CNTs cutting/fragmentation may occur. During the process, carboxylic and other oxygen-bearing groups are introduced onto CNTs surface, thus improving dispersion of CNTs. Similar effect can be obtained using ozone [62] (Fig. 11), Ar-O_2 plasma etching and flash-oxidation [36, 37].

Some oxidizing agents' behavior is different depending on the experiment. $KMnO_4$ is capable of carbon double-bond hydroxylation at room temperature, but when the solution is boiling, its oxidation capabilities are higher. When combined with sulfuric acid, very strong oxidizer Mn_2O_7 is generated, igniting almost every organic matter. This mixture is used to prepare phtalic acid from naphthalene.

Recent study thoroughly investigated efficiency of HNO_3 hydrothermal oxidation treatment for controllable surface oxidation on MWCNTs. It was shown that this method is more effective at introducing functional groups, while generating less carbon fragments, compared to common boiling method. [58]

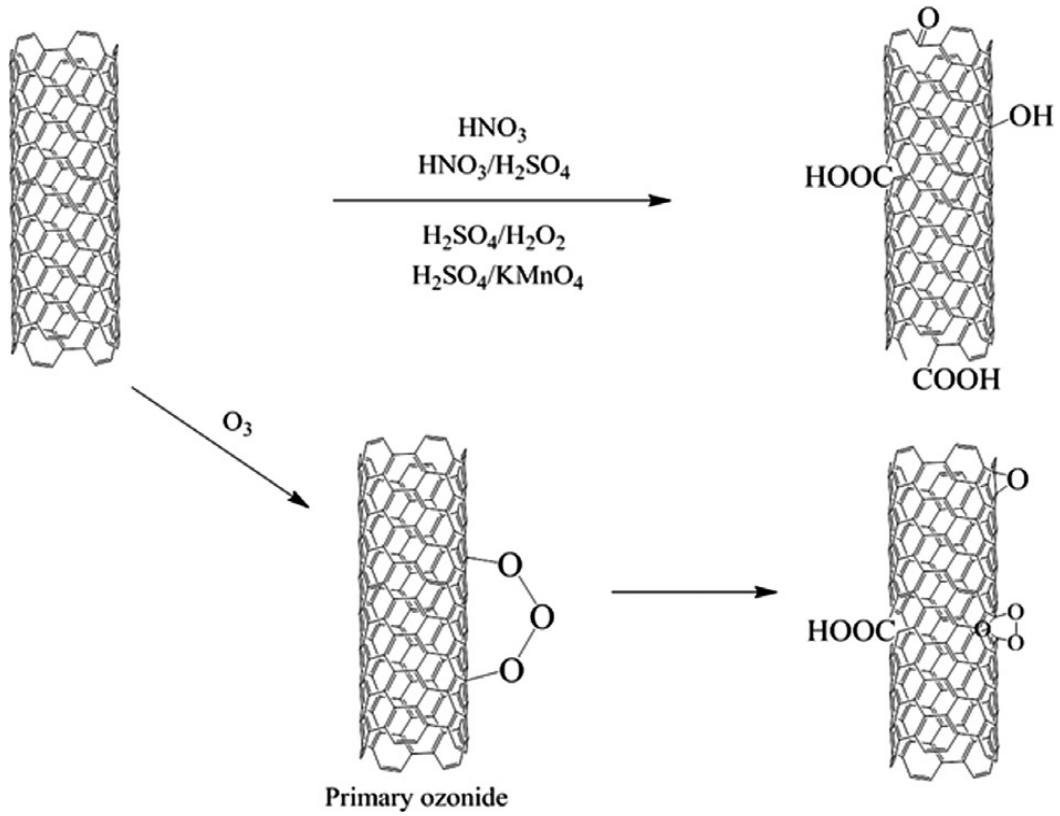

Fig. 11: Scheme of CNTs oxidation [63]

Fluorination is one of the first functionalization methods tested to directly introduce functional groups to nanotubes sidewall. Although electronic properties are significantly altered, morphology remains intact [64, 65]. Easily preparable F radicals are used as first step to introduce alkyl and aryl groups via lithium derivates (Fig. 12).

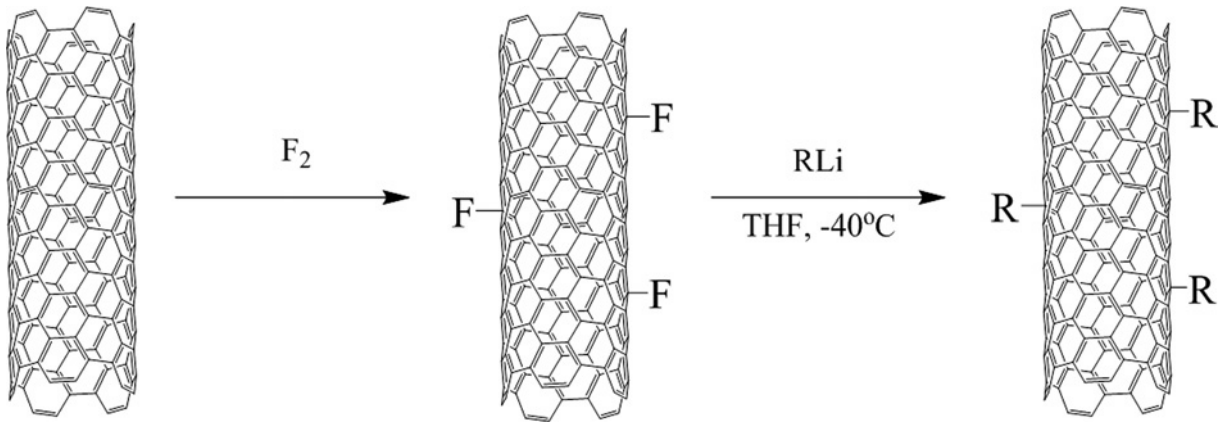

Fig. 12 Scheme of fluorination and consequent alkylation of CNT [63]

Another additive approach can be performed via nucleophilic dipyridyl imidazolidene that reacts with the electrophilic SWCNT π-system to give zwitterionic product (Fig. 13). This transfer of charge causes homogenous dispersion in aqueous solution, as electric repulsion forces are in effect [37, 65].

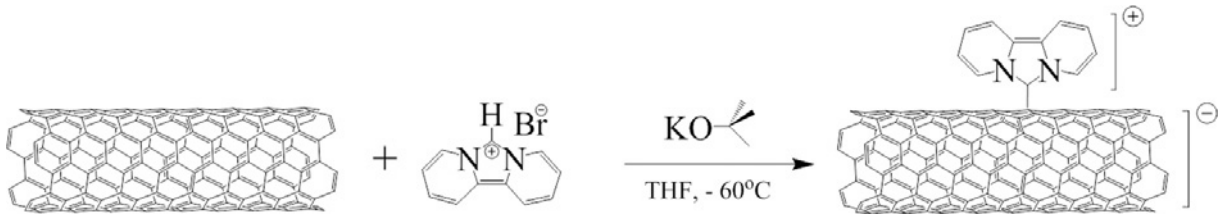

Fig. 13: Scheme of nucleophilic addition of dipyridyl imidazolidene to CNTs [63]

Electrophilic additions can also be performed using Lewis acid and halogen derivates. Electrophilic addition of trichloromethane also introduces chlorine into CNTs structure that can be hydrolyzed and then used to introduce other functional groups (Fig 14.) [63].

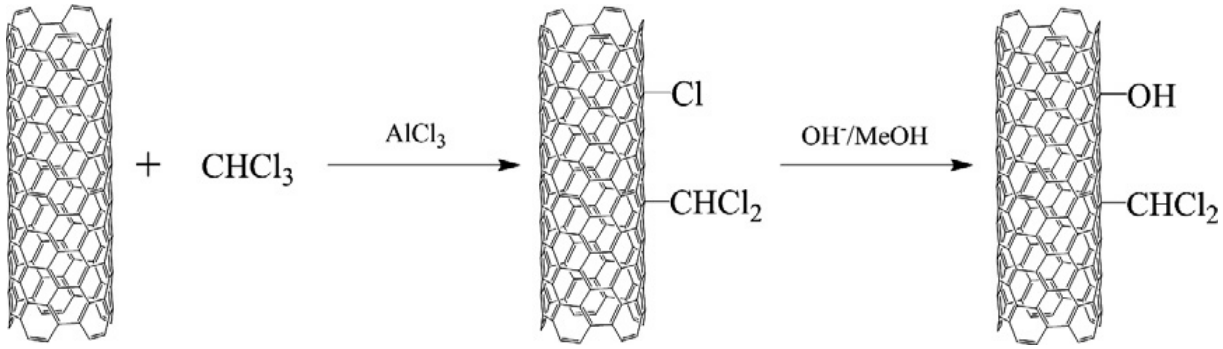

Fig. 14: Scheme of electrophilic addition on CNTs [63]

Methods described above serve as a first step in the complex modification technology. As primary functional groups are present, further derivatization might take place following general organic chemistry principles. At this stage it becomes easy to employ this knowledge. Some examples of additional procedures are described below.

Thiolation is an important method allowing preparation of CNTs-metal nanocomposites. Thiol group is well known for its interaction with metals, especially Au, thus enabling to create monolayer on Au surface. Nanocomposites prepared this way are used to develop antigen sensors for SPR (surface plasmon resonance) [66].

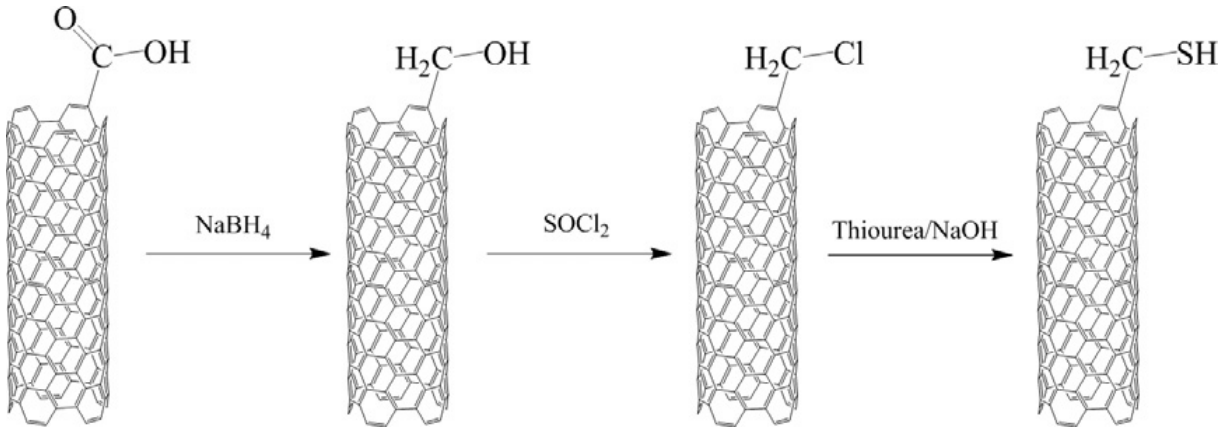

Fig. 15: Scheme of thiolation [63]

Amination is another methodology to introduce $–NH_2$ groups onto CNTs surface. There are few possible ways, for example Ar-NH_3 plasma treatment [67], substitution of –OH in carboxylic group (Curtius rearrangement), reduction of -NO_2 group, etc.

Carboxylic and amino groups can form peptide bond that is crucial for protein formation, thus –COOH and/or $–NH_2$ functional groups can serve as a vessel to covalently bond amino acids, proteins and other biological compounds. This feature enhances CNTs biocompatibility and allows one to develop new drug delivery methods or other medical applications.

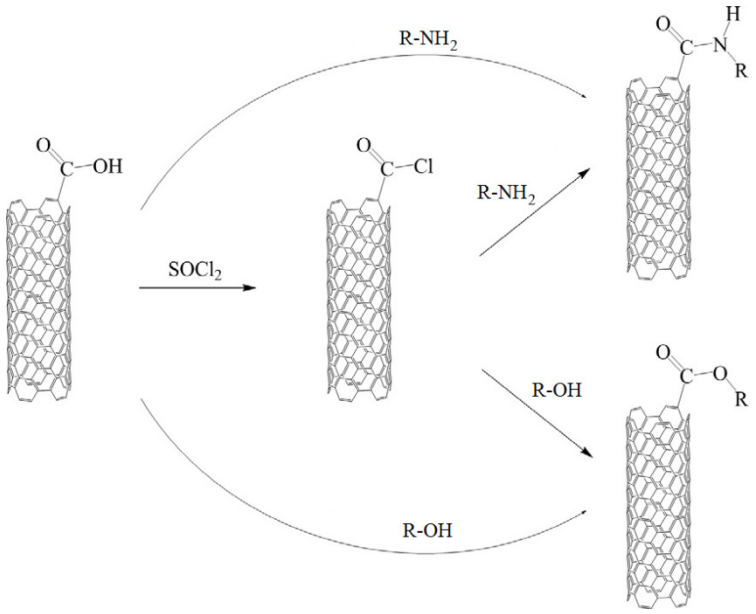

Fig. 16: Scheme of amidation and esterification of CNTs [63]

2.3.4 Non-covalent functionalization treatments

These methods to functionalize CNTs are well-known for their preservation of CNTs intrinsic structure. While covalent methods show high impact on electronic structure, these methods are interacting on the level of Van der Waals forces, thus changes induced are minor. Main goal of these treatment is to increase solubility in water, thus surfactant approach is applied. Surfactant is a compound consisting of both hydrophobic and hydrophilic parts, serving as a bridge between 2 incompatible environments.

CNTs delocalized electrons are positioned out of plane, making CNTs prone to form a π-π interaction. This interaction can be formed with C=C or aromatic core of the surfactant and due to its strength, it is advised to include at least one of these bonds into the chosen surfactant structure [4, 68].

Compounds used as surfactants can be broadly divided into 3 groups:

- Biomolecules
- Polymers
- Small compounds

Used compounds can also be divided by the covering way (Fig. 17):

- Adsorption
- Wrapping

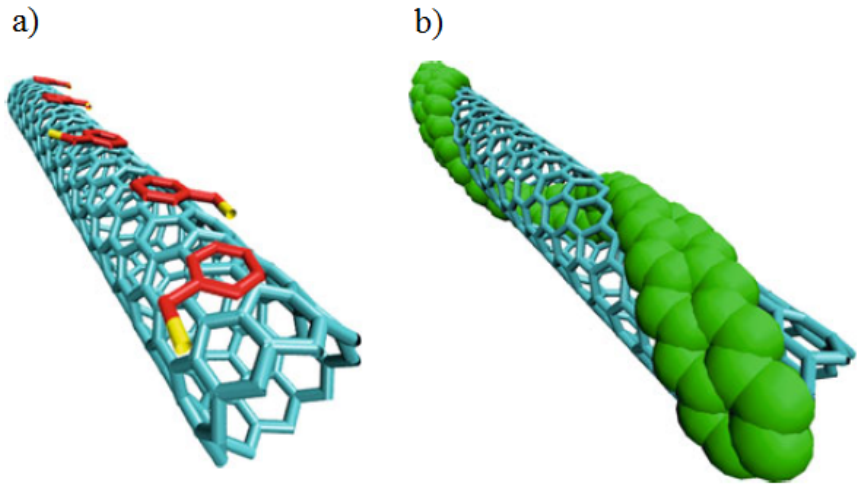

Fig. 17: Examples of (a) adsorption and (b) wrapping [23]

The first option to improve dispersibility is utilizing of surfactants. These molecules are relatively small compared to CNTs and are adsorbed onto CNTs surface with hydrophobic tail, while hydrophilic head remains detached and is facing into aqueous solution, reducing surface tension. Most used surfactants are for example SDS (sodium dodecyl sulfate) [69], SDBS (sodium dodecyl benzenesulfonate) [70], Tween 20, Tween 80 [71], Triton X-100 (octyl phenol ethoxylate) [70] and many more. Amount of surfactant needed for successful dispersion varies, as it is dependent on weight/surface ratio of CNTs. It has been demonstrated, that effectivity of the dispersion depends on surfactant concentration and thermal stability as well [71].

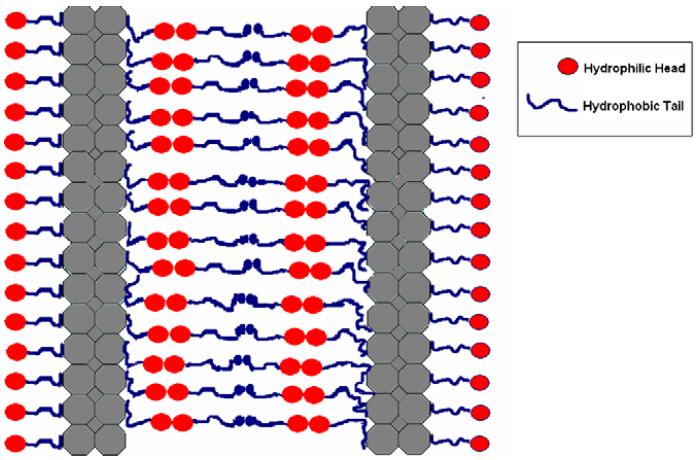

Fig. 18: Schematic representation of CNTs dispersion using surfactants [71]

Polymer based dispersions are principally the same as for surfactants. Most of the time, conjugated polymers are used for wrapping of CNTs, for example, poly(m-phenylene vinylene) (PmPV) or poly(3-hexylthiophene) (P3HT) [72]. These polymers are enhancing electronic properties of CNTs, however the stability and dispersibility in polar solvents is limited; thus block copolymers consisting conjugated and non-conjugated polymers that exhibit good solubility are used [63].

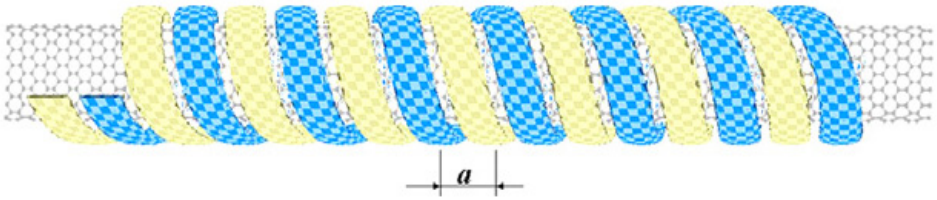

Fig. 19: Scheme of double helically-wrapped P3HT onto CNT with equally spaced coils [63]

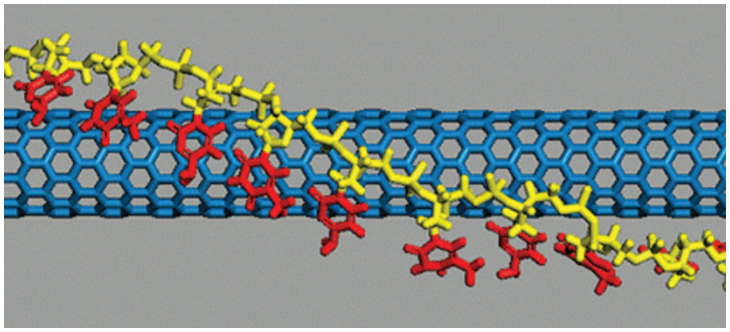

Fig. 20: Structural model of DNA-wrapped CNT [32]

Among vast number of possible choices from biomolecules, DNA attracted a lot of attention. This can be attributed to DNA being a “source code” of the life as we know it. Several attempts have been made to link CNTs and DNA, to form new biocompatible structures with possible self-assembly capabilities. During these experiments, high affinity of DNA towards CNTs have been discovered, thus applications using DNA to CNTs separation and functionalization started to develop. Most applications are using DNA in its single-stranded form (ss-DNA). It is assumed, that ss-DNA is capable to recognize/bind any given small molecule targets [49]. It has been demonstrated, that ss-DNA is wrapped around CNTs has planar bases stacked onto CNTs surface, while sugar negatively charged (deprotonated) backbone is facing outward, thus providing efficient dispersibility. Shorter DNA strands are also selective for specific chiral SWCNTs configurations and therefore are used for chiral selective separation [31, 50].

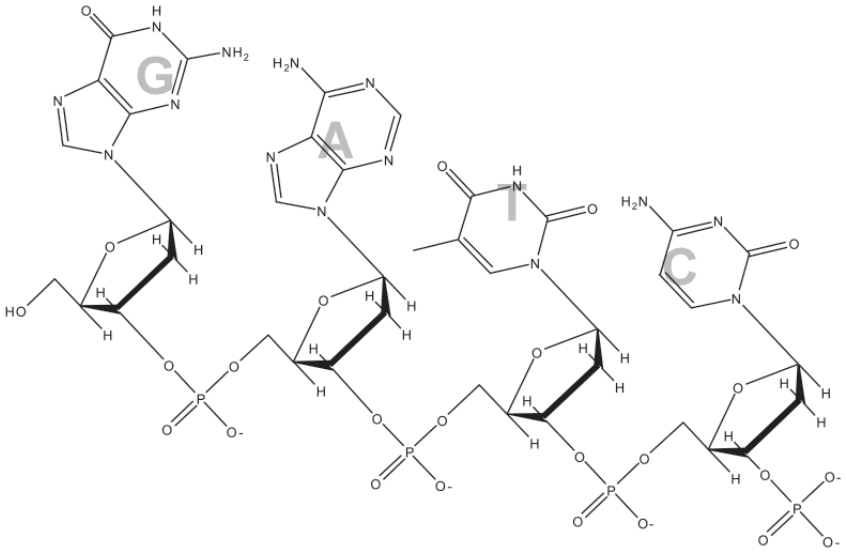

Fig. 21: Short oligonucleotide structure of guanine (G), adenine (A), thymine (T), cytosine (C), deoxyribose and a negatively charged phosphate group [32]

3 Practical part

This part of thesis contains information about experiments performed in laboratory, from preparation of samples, their analysis to final products' characterization and evaluation of theirs properties.

3.1 Treatment and functionalization of carbon nanotubes using selected methods

3.1.1 Chemicals, instrumentation and software used for the experiments

These materials were used for the experimental part:

- Nanocyl NC7000 (MWCNTs) – labeled as NC7K
- Nitric acid (HNO_3) – 65% p.a. (MACH chemikálie s.r.o.)
- Sulfuric acid (H_2SO_4) – 96% p.a. (MACH chemikálie s.r.o.)
- Hydrogen peroxide (H_2O_2) – 30% p.a. (MACH chemikálie s.r.o.)
- Sodium hypochlorite (NaOCl) – ~10% (Sigma-Aldrich)
- Potassium permanganate ($KMnO_4$) – powder (РЕАХИМ)
- Hydrochloric acid (HCl) – 36.5% (MACH chemikálie s.r.o.)
- DEMI water – 18.2 MΩ

These instruments were used for analyzes in experimental part

- Quanta FEG 450 (FEI) (SEM analysis)
- Tecnai F30 (FEI) (TEM analysis)
- XploRA™ (HORIBA Jobin Yvon) (Raman spectroscopy analysis)
- LECO RC612 (Carbon phase analysis)
- Nicolet 6700 FT-IR (Thermo Scientific) (FTIR analysis)
- STT-1700-12 (Sentro Tech Corp.) (Thermal annealing)

This software was used for experimental part

- MATLAB (R2010a)
- Accelrys Materials Studio 4.2

3.1.2 Methodology

In this chapter, methodology of samples preparation is described.

- F series of samples

The F series of samples was prepared by putting 0.3 g of NC7K into a flask. Subsequently stir bars and reagents were added and the flasks were placed on magnetic stirrers with heater and condensers were connected (for heated samples). Samples NC7K F1, F2, F4, F6 and F7 were then heated up to 70 °C for respective time (Tab. 1).

Tab. 1: F series experimental conditions

F series methodological data					
ID	mass [g]	Reagent	added mass/volume	added water	heated
NC7K F1	0.3	HNO_3	25 ml	-	for 8 hrs
NC7K F2	0.3	HNO_3	12.5 ml	12.5 ml	for 8 hrs
NC7K F3	0.3	$KMnO_4$	0.2 g	25 ml	not heated
NC7K F4	0.3	$KMnO_4$ + H_2SO_4	0.2 g + 5 ml	20 ml	for 8 hrs
NC7K F5	0.3	H_2O_2 + H_2SO_4	10ml + 15 ml	-	not heated
NC7K F6	0.3	$KMnO_4$	0.2 g	25ml	for 1 hour
NC7K F7	0.3	NaOCl	15 ml	10 ml	for 1 hour

At the next step, previously heated samples were cooled down to room temperature.

Samples NC7K F1-F5 were then still stirred for another 16 hours, while the rest were diluted, filtrated and washed to neutral pH.

After 16 hours, samples F1-F5 were also filtrated and washed to neutral pH. All samples were collected from the cake and dried at 60 °C for 12 hours on Petri dishes. Subsequently, dried samples were stored in rubber sealed vials.

- Sample NC7K ann (ann – annealed)

5 grams of NC7K were put into tubular furnace and the aperture was put together. At first, Ar gas bomb valve was opened, subsequently input and output furnace valves were opened as well. Gas was flushing through the furnace chamber for about 5 minutes (to flush out air), after that the furnace heating was initiated. Target temperature was set to 600 °C, ramping 120 °C/hr, hold time for 2 hours and then cooling down back to room temperature. Sample was then collected to rubber sealed vial.

- Sample NC7Kp (p – purified)

10 grams of NC7K were put into flask and 150 ml of DEMI water was added. Subsequently, 50 ml of H_2O_2 and 100 ml of HCl was added. The mixture was stirred for 3 hours and then filtered to neutral pH. At the next step, the filtration cake was collected and put into another flask with 150 ml of DEMI water. The mixture was stirred and 150 ml of HNO_3 was added. The procedure continued by stirring for another 3 hours. Sample was then filtered to neutral pH and dried at 80°C overnight and stored in rubber sealed vial.

This sample was originally prepared for another project; however I considered it useful to include it in this thesis.

3.2 Characterization of treated products

3.2.1 Summary of properties published by manufacturer [73]

Tab. 2: Properties of NC7000 product

Property	Unit	Value	Method of measurement
Average diameter	nanometers	9.5	TEM
Average length	microns	1.5	TEM
Carbon purity	%	90	TGA
Metal oxide	%	10	TGA
Amorphous Carbon	-	*	HRTEM
Surface area	m^2/g	250-300	BET

* Pyrolytically deposited carbon on the surface of the NC7000

3.2.2 Electron microscopy

SEM was used to obtain insight on morphology of samples and EDS was performed to analyze elemental composition. Further analysis of NC7K was conducted using TEM (Fig. 22), to obtain information of CNTs radius and to estimate number of walls presented.

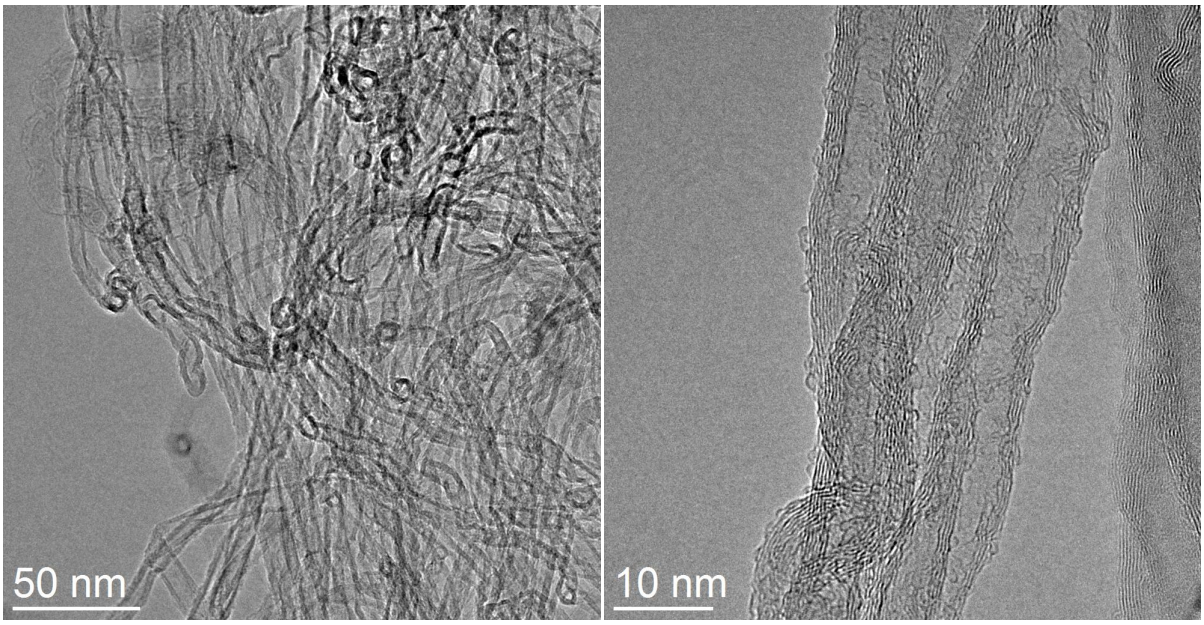

Fig. 22: TEM images of pristine NC7000

According to TEM images, a radius of NC7K nanotubes is approximately 10 nm, with almost no amorphous carbon. Number of walls is about 7. These results are in good agreement with data provided by manufacturer (Tab. 2). As the amount of amorphous carbon is very low, it can be assumed that manufacturer applied some purification treatment. An email had been send to the company asking for clarification, but no reply has been received yet.

- NC7K

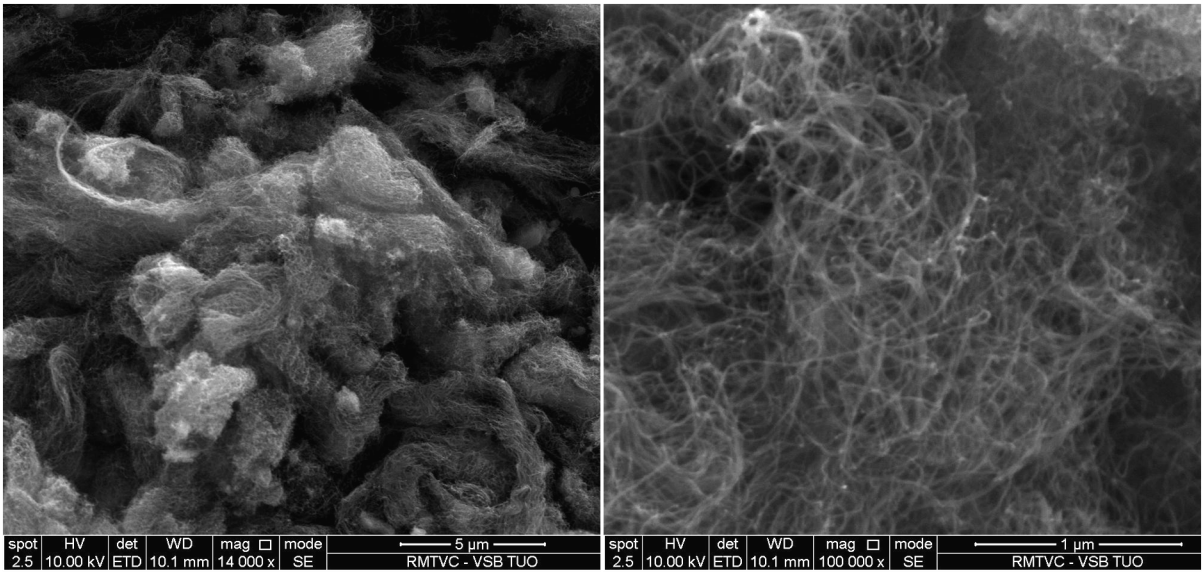

Fig. 23: SEM images of NC7K sample

- NC7Kp

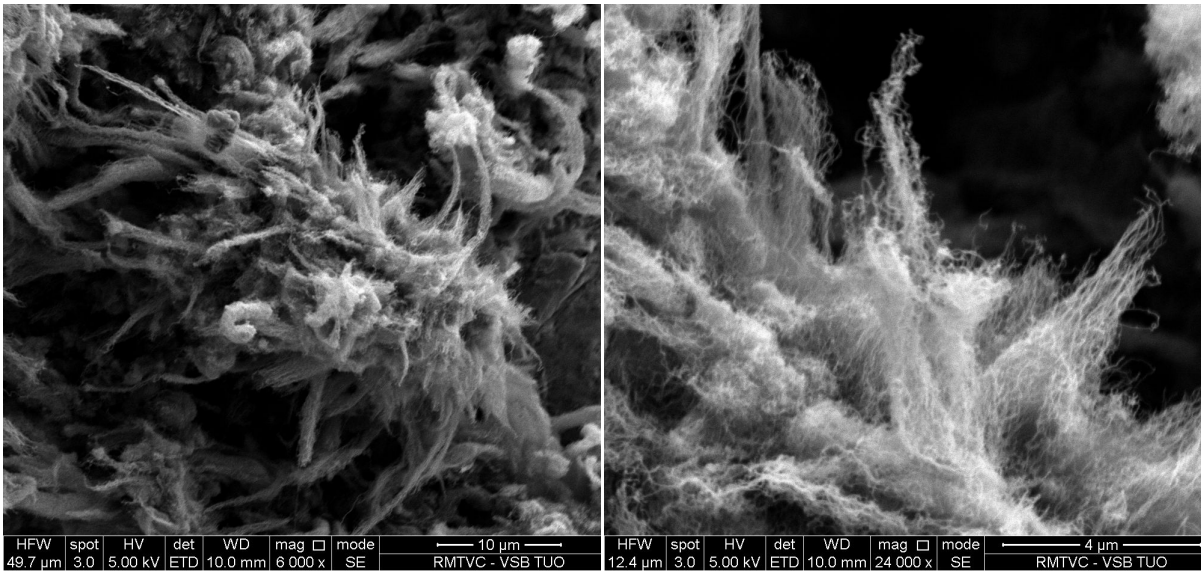

Fig. 24: SEM images of NC7Kp sample [74]

- NC7K F1

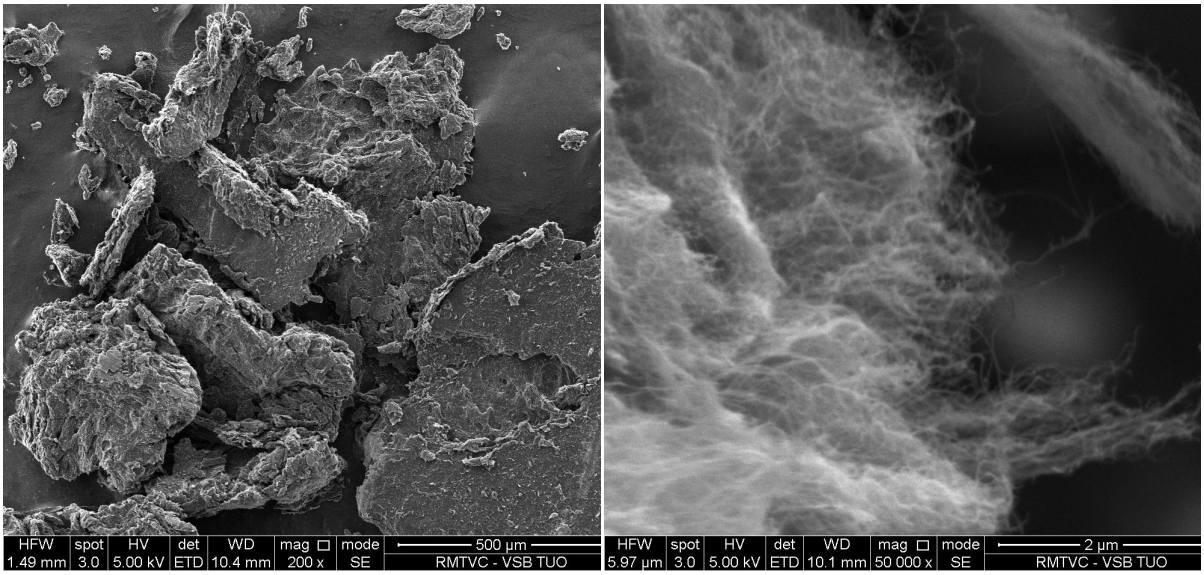

Fig. 25: SEM images of NC7K F1 sample

- NC7K F3

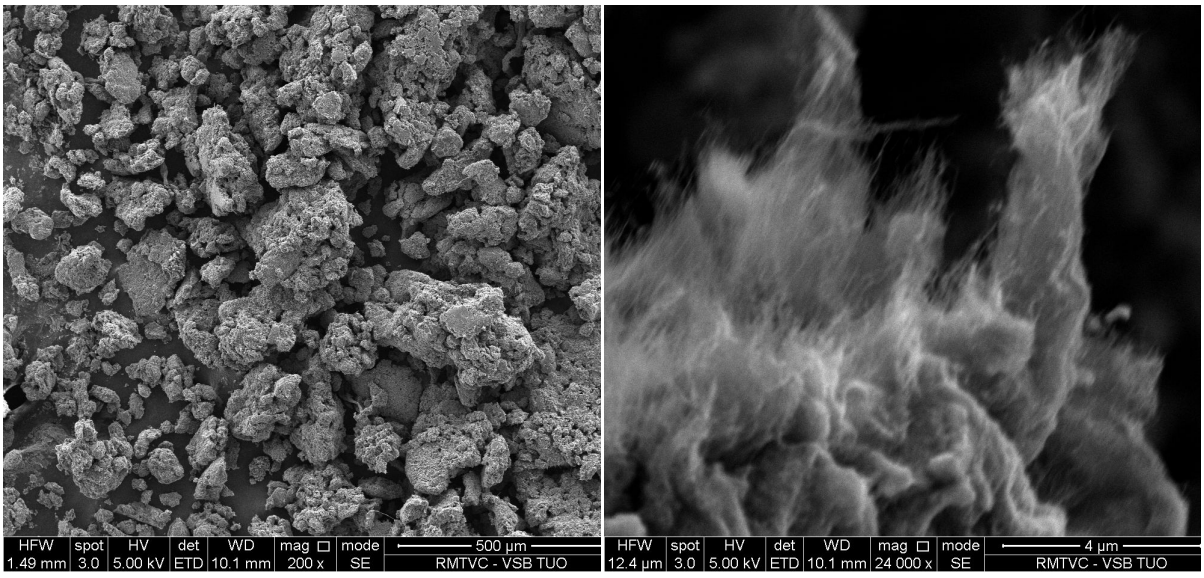

Fig. 26: SEM images of NC7K F3 sample

- NC7K F4

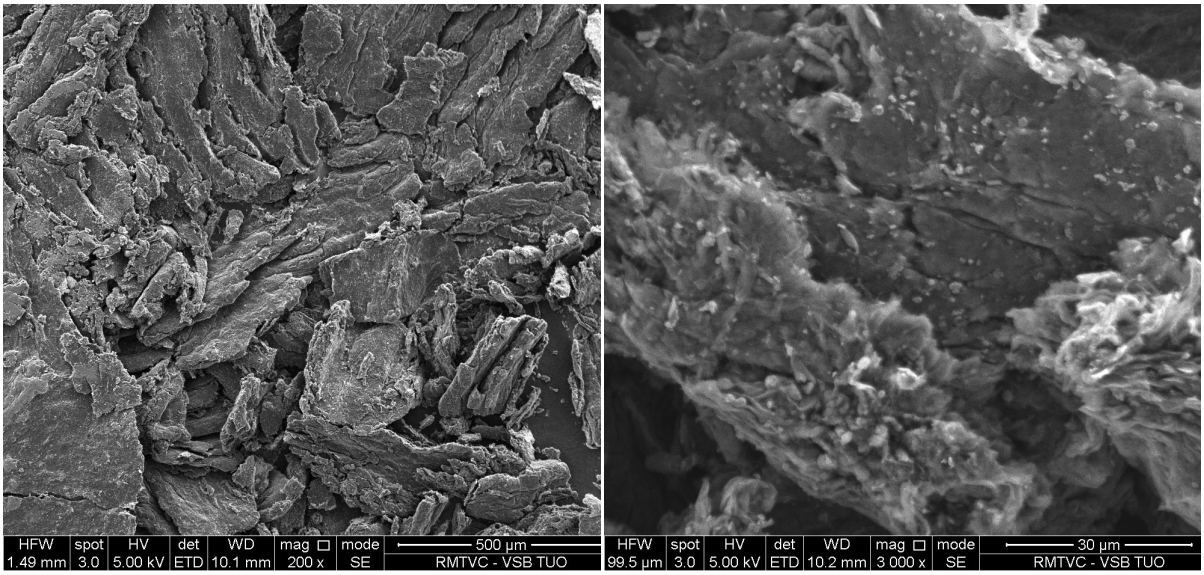

Fig. 27: SEM images of NC7K F4 sample

- NC7K F5

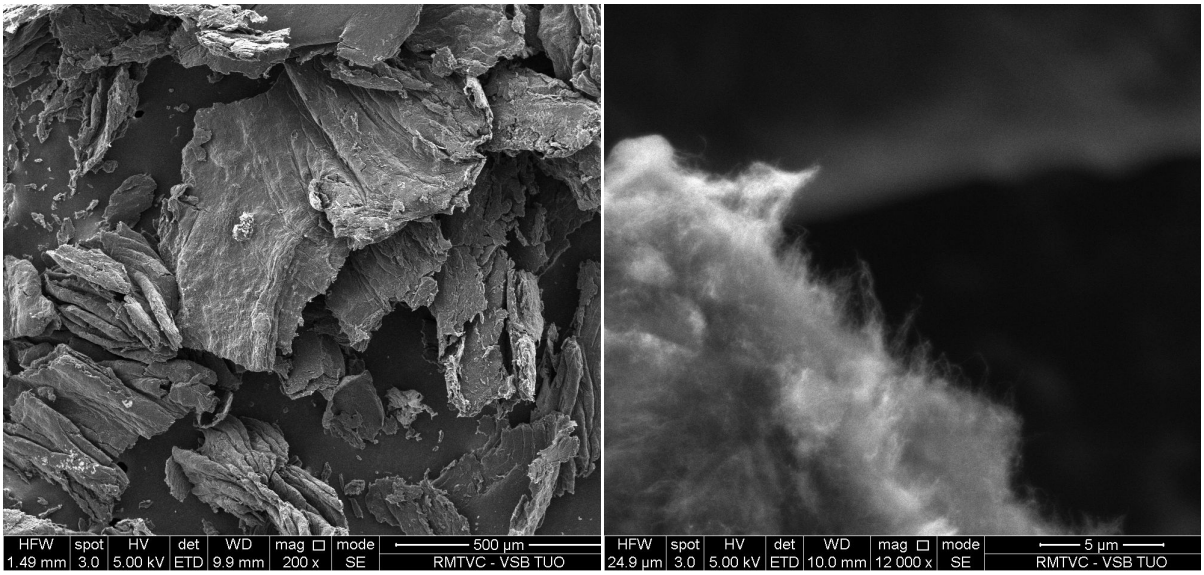

Fig. 28: SEM images of NC7K F5 sample

- NC7K F6

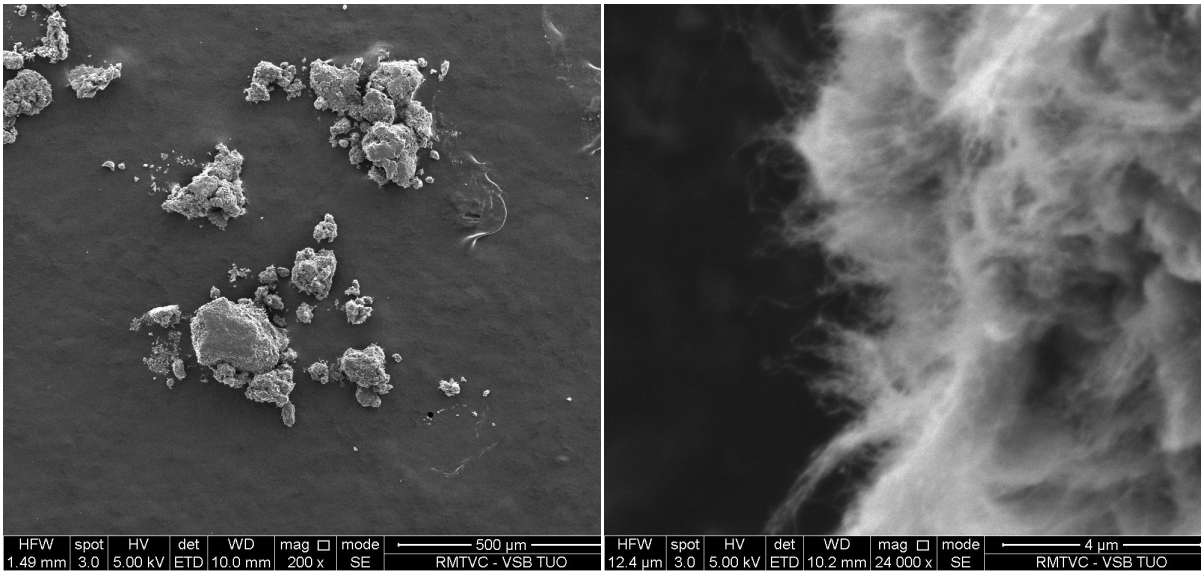

Fig. 29: SEM images of NC7K F6 sample

- NC7K F7

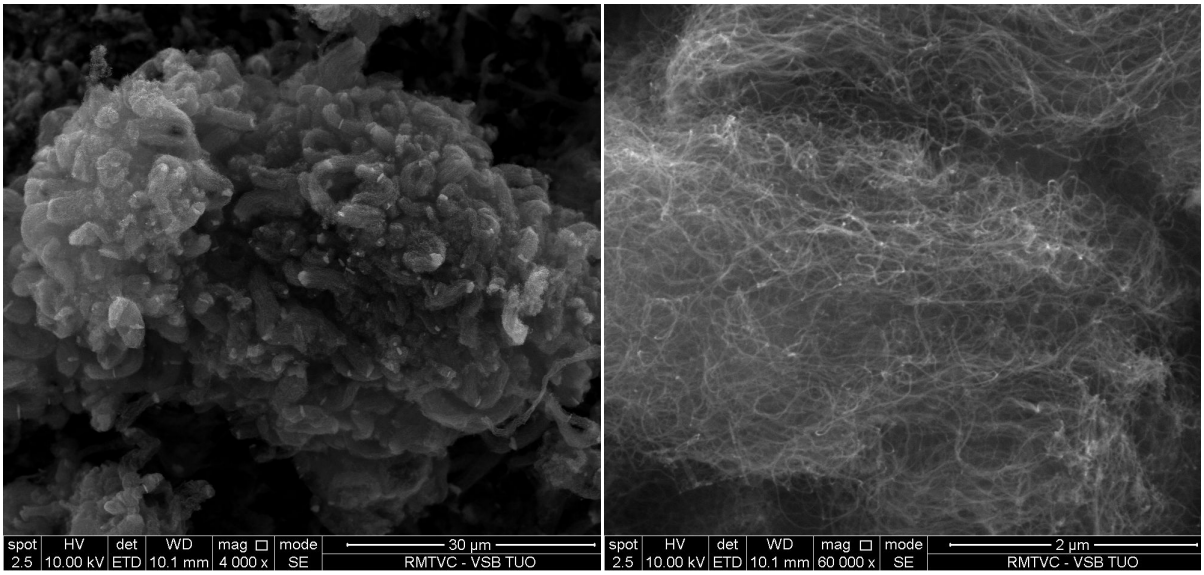

Fig. 30: SEM images of NC7K F7 sample

From the SEM images it can be seen, that samples NC7Kp (Fig. 24) and NC7K F7 (Fig. 30) are having similar entanglement of CNTs as pristine NC7K sample (Fig. 23). This might be due to lower amount of oxidation, thus sufficient dispersion and reaggregation (during drying) was not taking place.

Samples F3 (Fig. 26) and F6 (Fig. 29) are showing different aggregates compared to pristine nanotubes. The bundles showed are looking like porous material, probably caused by residual crystallized MnO_2 present on the surface. These crystals are probably serving as zones for water vaporization during drying, thus creating these pores.

Samples F1 (Fig. 25), F4 (Fig. 27), F5 (Fig. 28) are showing sheet-like structure of aggregates, suggesting sufficient dispersibility of samples in water to rearrange structure of aggregates. Vaporization of water during drying went through the whole volume. Sheets were formed on Petri dishes during drying, as the layers of samples were thin and cracky.

All functionalized samples that were analyzed show "hairy" nanotubes compared to pristine material, thus indicating successful modification of CNTs surface.

Samples NC7K F2 and NC7K ann were not analyzed, as sample F2 is expected to look similar to sample F2 (analogous treatment) and sample NC7K ann should preserve the same morphological characteristics of NC7K (not dispersed in water).

EDS analysis showed major presence of Al (Al_2O_3 catalyst used for CNTs production). Samples F3 and F6 are having Mn present (in form of MnO_2) as well (figures not shown).

3.2.3 Raman spectroscopy

Raman spectroscopy analysis was performed to assess structural integrity of CNTs before and after respective treatment. From this point of view, we are looking for I_G/I_D ratio, as it is generally used for evaluation of damage done to sp^2 carbon. Numerical data were exported and processed in MATLAB. Background was corrected manually.

As we can see in Fig. 31, Raman spectra of samples are mostly identical. This result supports statement presented in publications, that Raman spectroscopy is less powerful to assess structural defects in already defective material (in this case MWCNTs) and is more suitable for SWCNTs assessment. The D band can be seen at 1348 cm^{-1}, G band at 1590 cm^{-1} and 2D band at 2688 cm^{-1}. RBM band is not present (as expected).

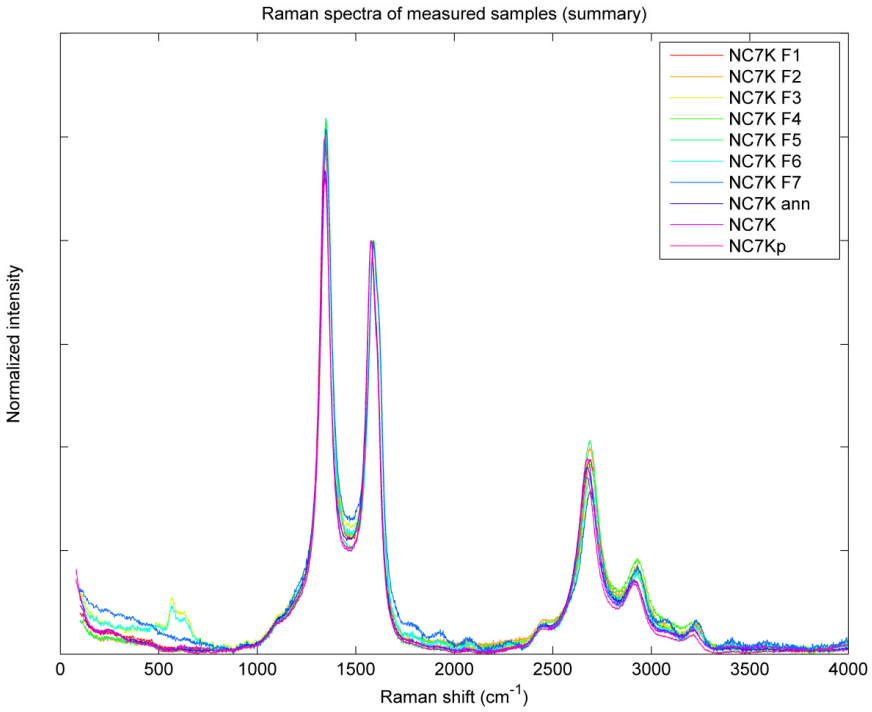

Fig. 31: Raman spectra of analyzed samples

Samples NC7K F3 and NC7K F6 also have new peaks present (564 cm^{-1}, 631 cm^{-1}). These peaks were identified as residual MnO_2, indicating its improper removal from samples [75].

Respective I_G/I_D ratios of samples are presented in Tab. 3.

Tab. 3: I_G/I_D ratios of analyzed samples

Sample	I_G/I_D
NC7K	0.87
NC7Kp	0.80
NC7K F1	0.81
NC7K F2	0.80
NC7K F3	0.79
NC7K F4	0.77
NC7K F5	0.77
NC7K F6	0.80
NC7K F7	0.79
NC7K ann	0.86

3.2.4 FTIR

FTIR analysis of samples was performed using KBr pellet method, with ~ 0,5 mg of sample and 260 mg of spectrocopy-grade KBr. As weighing CNTs samples is not accurate enough at these small quantities, FTIR spectra are normalized with the intensity of the C–H band at 2919 cm^{-1} [22]. Samples are divided into groups for clarity (Fig. 32 – 35). Respective bands are included in figures. Possible vibrations are demonstrated on SWCNTs model for enhanced comprehension (grey – carbon, red – oxygen, white – hydrogen).

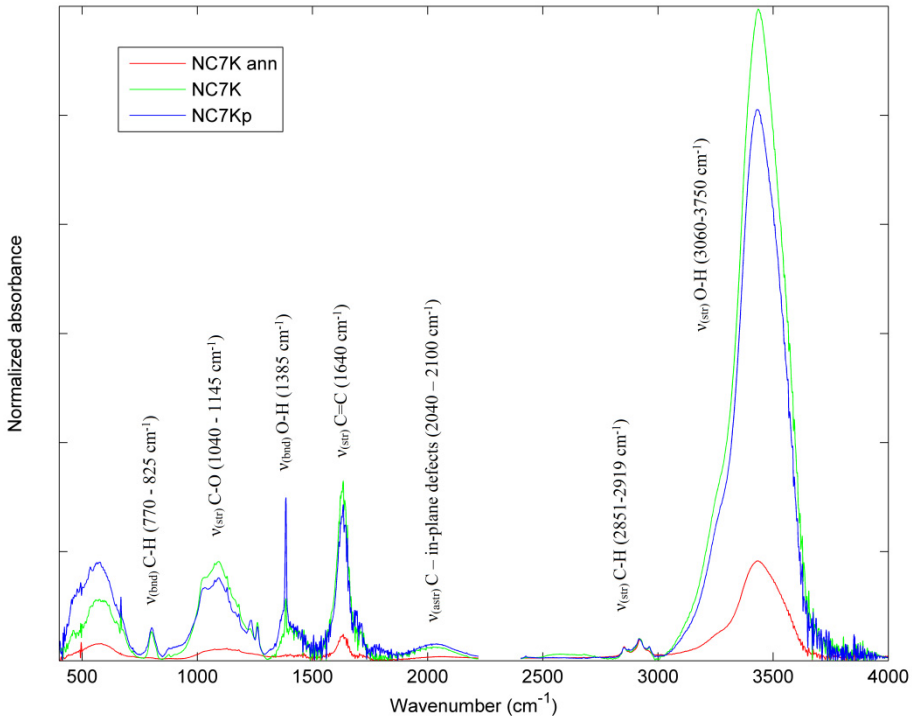

Fig. 32: FTIR spectra of pristine, annealed and purified CNTs

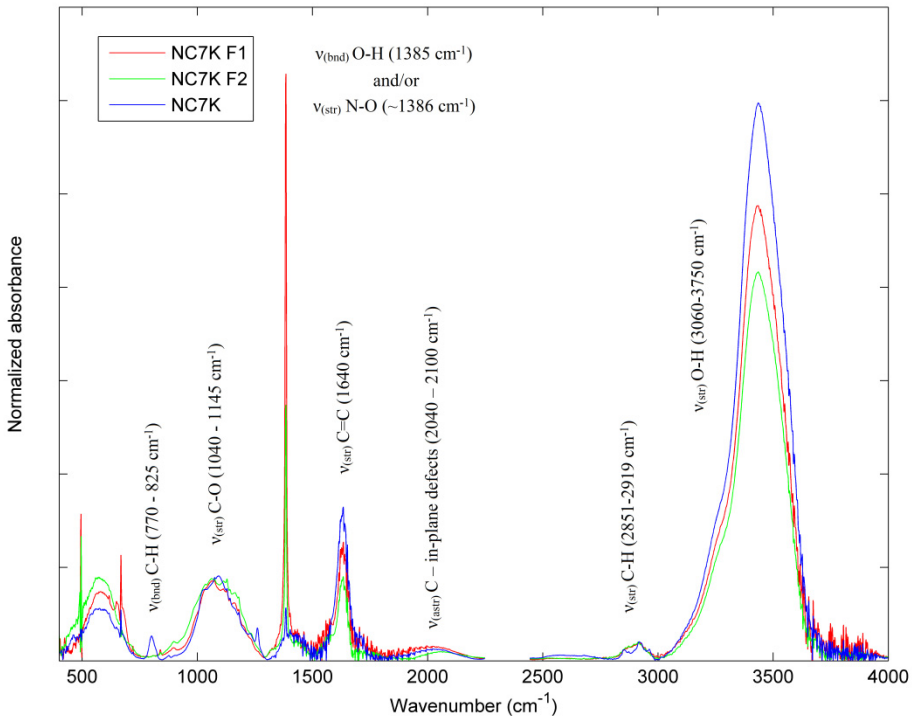

Fig. 33: FTIR spectra of samples treated with nitric acid

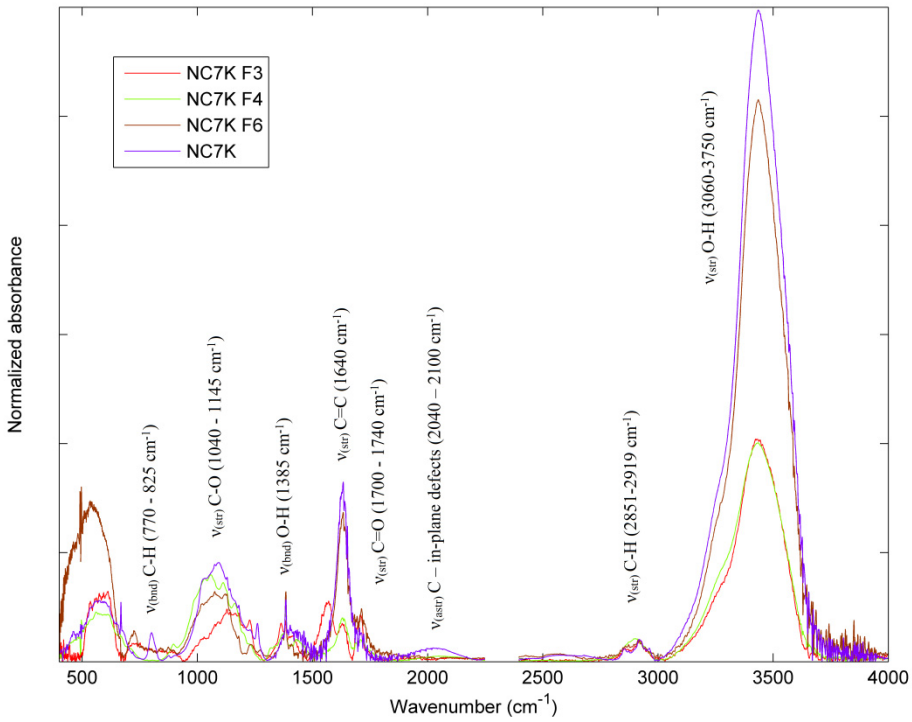

Fig. 34: FTIR spectra of samples treated with potassium permanganate

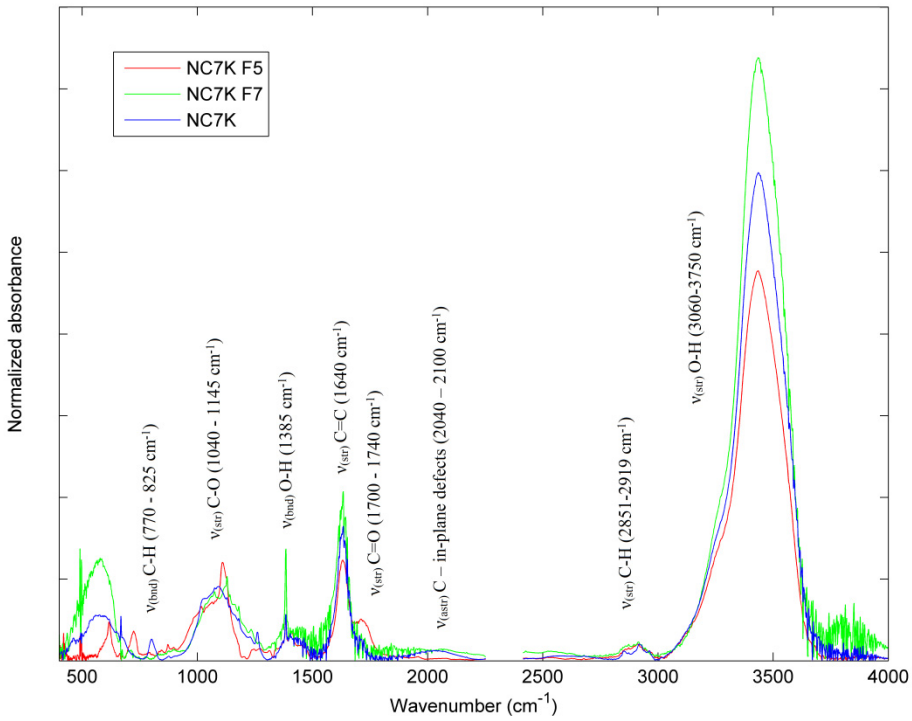

Fig. 35: FTIR spectra of samples treated with hydrogen peroxide and sodium hypochlorite

From the results we can see, that thermal annealing significantly lowered intensity in all bands, thus indicating that pristine nanotubes are already oxidized a little bit. Annealing also reduced amount of defects (as structurally perfect CNTs are IR inactive).

Each band (except the one presenting broad O-H stretching) is visualized using exemplar model of oxidized SWCNT for better clarity. Real model of MWCNT would be computationally expensive and not synoptic enough.

Broad band of O-H stretching vibrations (3060 – 3750 cm^{-1}) includes wide variety of hydrogen bond interactions as well as possible moisture, thus it cannot be solely used to evaluate the grade of oxidation.

The band presenting C-H stretching vibrations (2851 – 2919 cm^{-1}) is used for normalization of spectra received and serves to compare the oxidation efficiency.

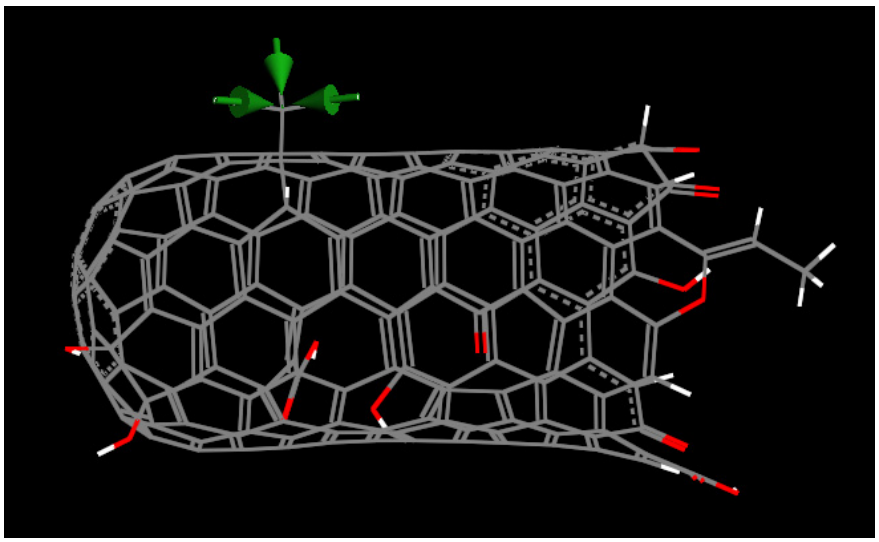

Fig. 36: Model of SWCNT with C-H stretching vibration

Small band (2040 – 2100 cm^{-1}) was identified as defects of carbon network in CNTs. This conclusion was made from molecular dynamics simulation performed on oxidized SWCNT model. This stretching was localized on the area of SWCNT, where pentagon-heptagon exist with no other element bonded. As this stretching is in-plane, it can be assumed, that similar stretching can occur in MWCNTs.

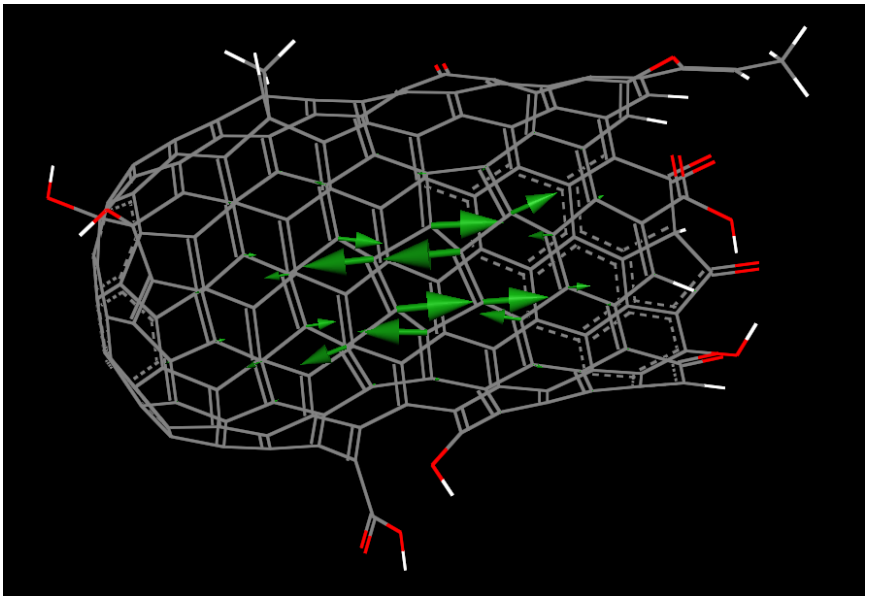

Fig. 37: Model of SWCNT with C-defects stretching vibration

Weak band representing C=O stretching (1700 – 1740 cm^{-1}) is presented in samples NC7K F3, F5 and F6, indicating presence of carboxylic groups.

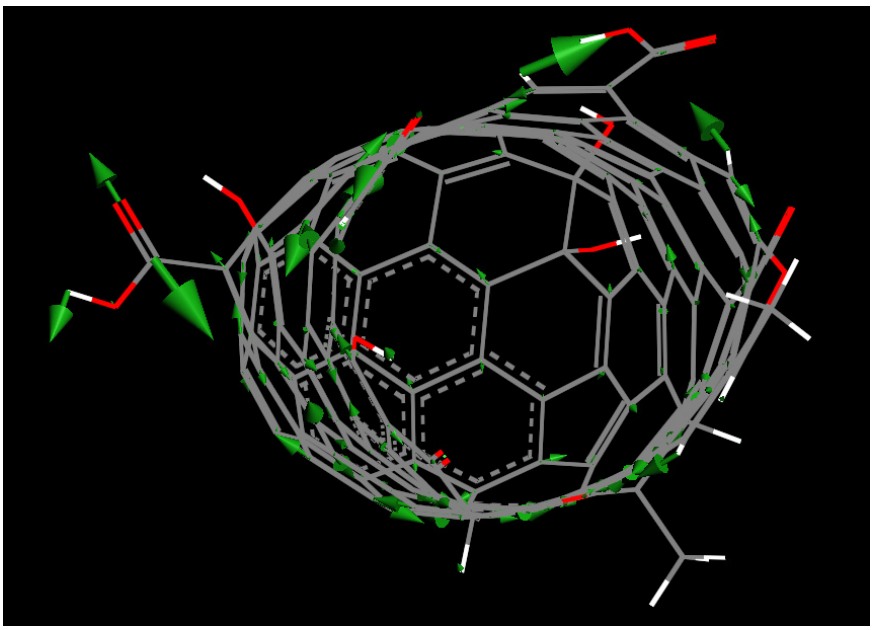

Fig. 38: Model of SWCNT with C=O stretching vibration

Medium band presenting C=C stretching (~1640 cm^{-1}) is mainly originated from unsaturated carbon in CNTs structure.

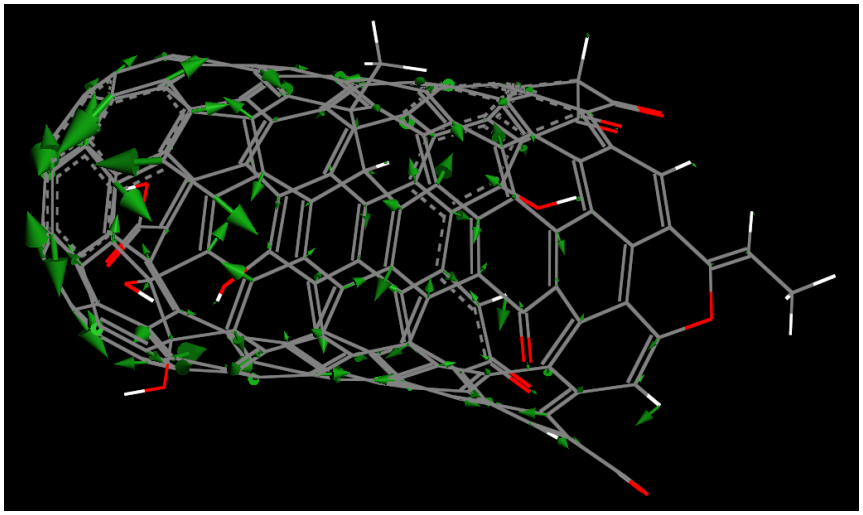

Fig. 39: Model of SWCNT with C=C stretching vibration

Strong band of O-H bending (1385 cm^{-1}) is used as a main indicator of oxidation. The strongest presence of this band is in samples F1 and F2, indicating that treatment with HNO_3 might be promising. After investigation of results from carbon phase analysis,

this band probably represents N-O stretching of nitro group as well, as other samples not treated with HNO_3 also have this band present. This unfortunate blending makes it then hard to estimate the ratio of –OH and $–NO_2$ groups in the sample, thus requiring another analysis [76].

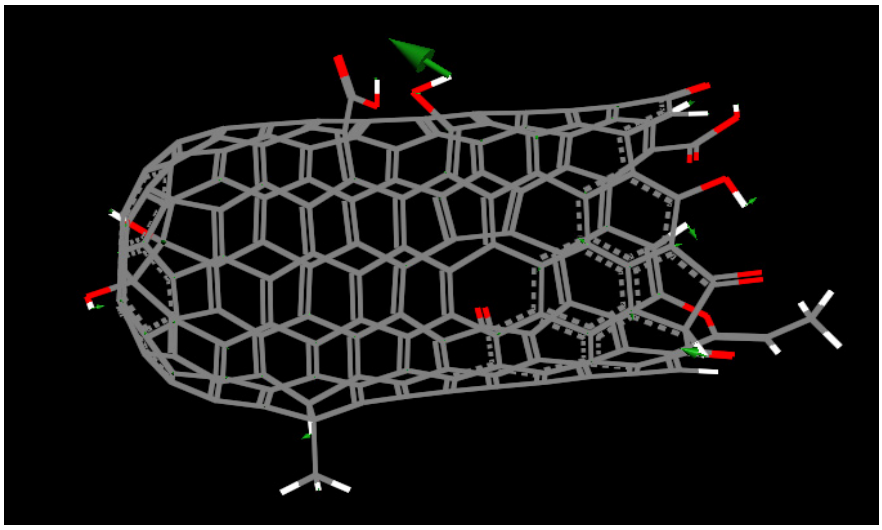

Fig. 40: Model of SWCNT with O-H bending vibration

Band of C-H bending (770 – 825 cm^{-1}) is unchanged across all samples except NC7K ann sample. It is expected, as C-H stretching band is used for normalization.

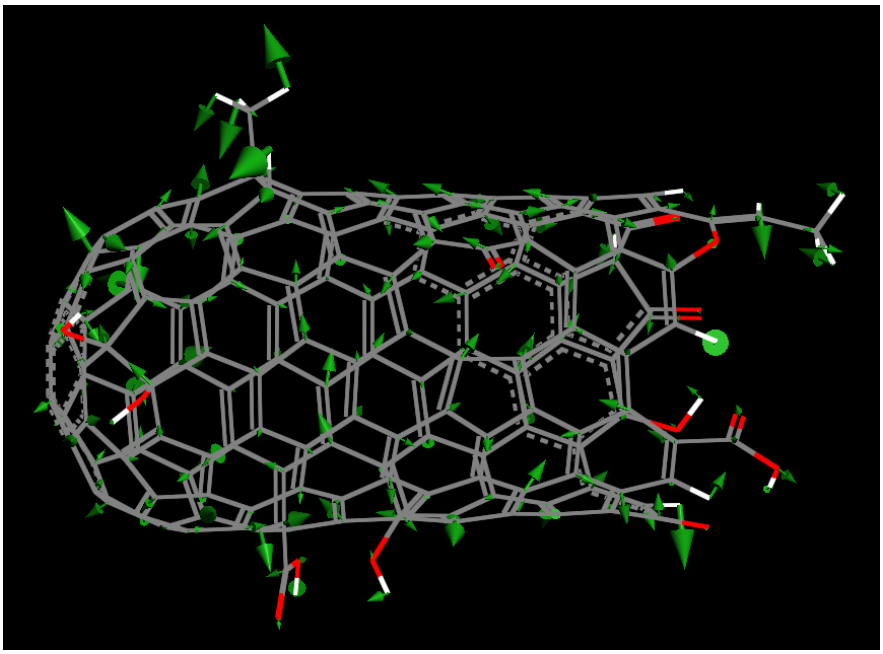

Fig. 41: Model of SWCNT with C-H bending vibration

The conclusion from FTIR analysis is that treatments using HNO_3 are probably most successful in CNTs oxidation (blending with $–NO_2$), although C=O groups were undetected. On the contrary, treatments using $KMnO_4$ and combination of sulfuric acid with hydrogen peroxide seem to be successful in the introduction of carboxylic groups on CNTs surface, while the amount of hydroxylic groups is rather small. This might be due to low amount of sample used for analysis as the sample itself could be inhomogeneous, thus analysis might be inaccurate.

3.2.5 Carbon phase analysis

Carbon phase analysis was performed on LECO RC612. This method was implemented to evaluate absolute amount of carbon and hydrogen in each sample. Oxygen was selected as a flushing gas (unfortunately, nitrogen is not yet installed).

Calibration of the machine was performed by the instructions in the operational manual, using provided standards. Analysis method was manually created after some test runs on pristine NC7000 samples. The analysis procedure was following these steps:

- Heating up catalysts (750 °C) and furnace (100 °C) after start-up (optional).
- Burn-off procedure (thermal desorption of CO_2 and water from quartz vessels at 1000 °C in furnace).
- Preparation of samples (weighing) and cooling down the furnace (100 °C).
- Initiation of analysis (weight input and analysis method selection) and waiting for signal to put sample into the furnace (prompts user to launch analysis itself).
- Waiting for stabilizing IR detectors. (Software itself performs checking of detectors stability, but stabilization of H_2O detector takes longer time than CO_2. It seems that software prioritizes carbon analysis, thus launching analysis at the time software prompts the user, H_2O detector might still not be stable. Due to this rushing, H_2O results might be incorrect).
- Confirmation of the prompt and insertion of the quartz vessel with sample into the furnace.
- Waiting for analysis to finish, removing vessel with residuals to cool it down and then weighing residuals in the vessel. Furnace automatically cools down to stand-by temperature (100 °C in this case)

After the analysis, raw numerical data were exported and processed using MATLAB.

Carbon data can be presented as received, while analyzed water data are recalculated to corresponding hydrogen.

As majority of samples were having similar dependency, only some images are included. All results obtained are then presented in Tab. 4 and 5.

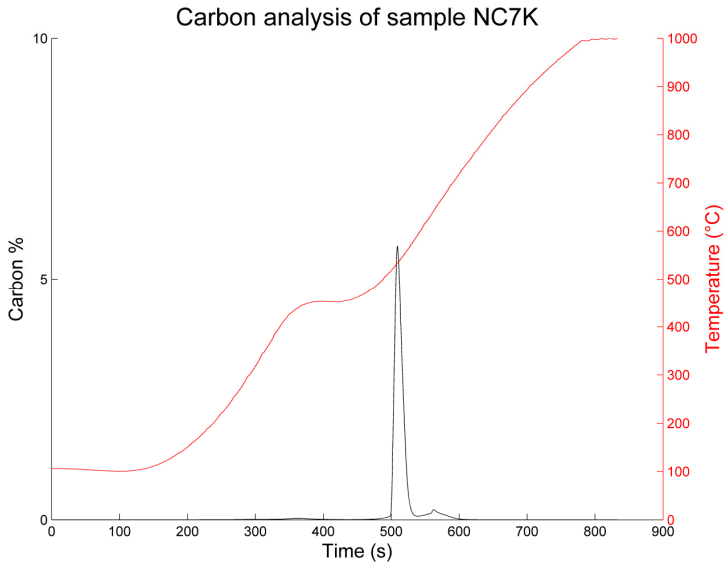

Fig. 42: Carbon analysis of NC7K sample

The amount of hydrogen in NC7K and NC7K ann samples was below detection limit, thus indicating very low grade of oxidation. Amorphous/damaged carbon starts to burn out at 370 °C, CNTs' carbon at approx. 490 °C (Fig. 42). Similar dependency was detected for all samples except NC7K F3, F6 and F7. In these samples the amorphous/damaged and CNTs' carbon part becomes blended and the burn out itself starts at approx. 210 °C (Fig. 43). This decrease in thermal stability is a consequence of MnO_2 present (samples NC7K F3 and F6), while in NC7K F7 the highly disrupted structure might be the cause.

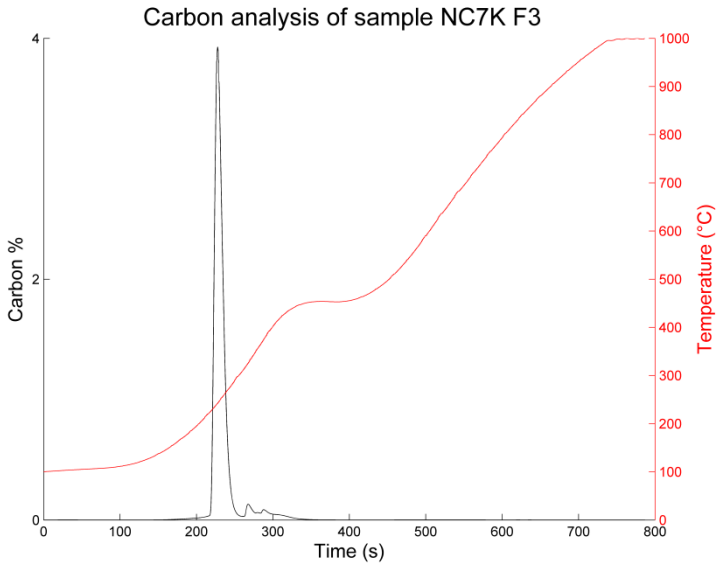

Fig. 43: Carbon analysis of NC7K F3 sample

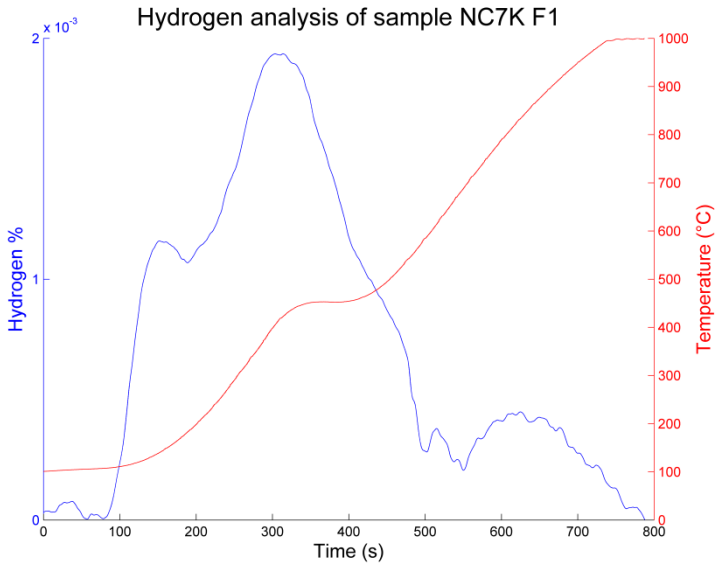

Fig. 44: Hydrogen analysis of NC7K F1 sample

The results of hydrogen analysis are showing minor moisture contribution, while the major amount of hydrogen becomes burnt out from sample at temperatures about 300 – 350 °C (Fig. 44), similar to amorphous/functionalized carbon temperatures. Samples with blended peaks are having hydrogen peaks blended in similar manner (Fig. 45).

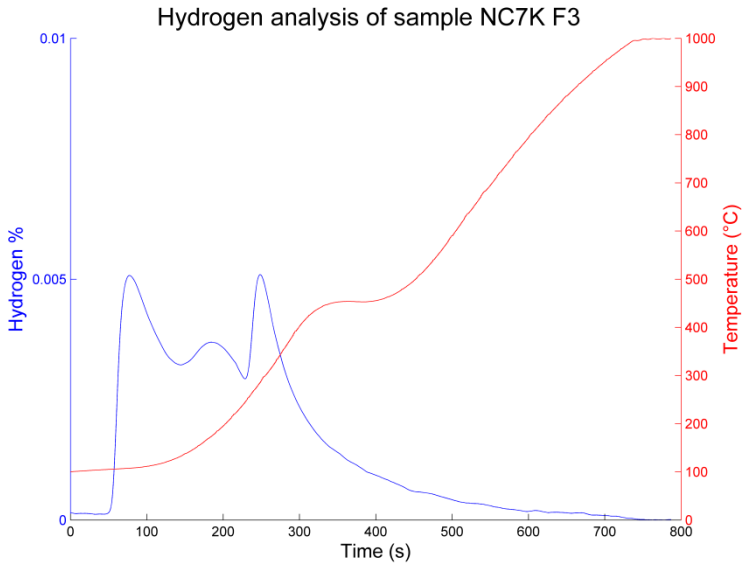

Fig. 45: Hydrogen analysis of NC7K F3 sample

Tab. 4: Carbon phase analysis results

Carbon phase analysis results						
Sample	Amorphous/damaged carbon	CNTs carbon	Total carbon	Hydrogen	Residuals	Other
	% (δ = 0.05%)					
NC7K	2.23	86.32	88.55	-	11.3	0.15
NC7Kp	1.89	87.43	89.32	0.24	8.50	1.94
NC7K F1	5.12	78.83	83.95	1.52	5.30	9.23
NC7K F2	4.18	83.32	87.50	0.96	6.50	5.04
NC7K F3	-	56.53	56.53	0.92	34.4	8.15
NC7K F4	7.43	76.07	83.50	0.54	12.2	3.76
NC7K F5	1.88	92.99	94.87	1.32	1.90	1.91
NC7K F6	-	56.06	56.06	1.17	40.4	2.37
NC7K F7	-	84.88	84.88	0.99	13.4	0.73
NC7K ann	2.17	86.45	88.62	-	11.3	0.08

Tab. 5: Recalculated carbon phase analysis results (residue-free)

Carbon phase analysis results (recalculated on 0% residuals)					
Sample	Amorphous/damaged carbon	CNTs carbon	Total carbon	Hydrogen	Other
	% (δ = 0.05%)				
NC7K	2.51	97.32	99.83	-	0.17
NC7Kp	2.07	95.55	97.62	0.26	2.12
NC7K-F1	5.41	83.24	88.65	1.61	9.75
NC7K-F2	4.47	89.11	93.58	1.03	5.39
NC7K-F3	-	86.17	86.17	1.40	12.42
NC7K-F4	8.46	86.64	95.10	0.62	4.28
NC7K-F5	1.92	94.79	96.71	1.35	1.95
NC7K-F6	-	94.06	94.06	1.96	3.98
NC7K-F7	-	98.01	98.01	1.14	0.84
NC7K-ann	2.45	97.46	99.91	-	0.09

From the results (Tab. 4 and 5) it can be seen, that samples NC7K F1, F5 and F6 are showing the highest hydrogen presence (in respective order), while sample NC7K F4 CNTs' structure is the most damaged one.

If the results are recalculated to ideal 0% impurity presence, NC7K F6 sample is the one with highest hydrogen content; followed by samples F1, F3, F5 and F7. To ensure removal of these metallic impurities, additional HCl treatment is required.

It can only be speculated that unidentified portion of the sample (labeled "Other") is oxygen, as the reagents used are not expected to introduce other elements not present in solid residue after analysis. Results from FTIR are indicating presence of C=O group in samples NC7K F3, F5 and F6 so the possibility of this being oxygen is high. However this band was not found in samples NC7K F1 and F2, suggesting very much possible existence of $–NO_2$ groups.

3.3 Discussion and proposition of methodological procedures

For the experimental part, series of samples were prepared using commonly used oxidizers. All samples were analyzed by well-established methods in this research field – scanning and transmission electron microscopy, Raman spectroscopy and FTIR analysis. Another conventional method is TGA (thermogravimetric analysis) suitable for many materials; instead the decision was made to use carbon phase analysis instead.

Benefits of this choice are self-explanatory; TGA is able to provide sample weight dependency on temperature/time, while carbon phase analysis provides dependency of carbon and hydrogen (or oxygen with nitrogen used as flushing gas) on temperature. As functionalization treatments were simple and their goal was oxidation of CNTs, carbon phase analysis is able to measure composition of almost every burnable element in CNTs. Residuals can be weighed as well as in TGA, giving information about metal catalysts portion. Another problem with TGA is the amount of time necessary to analyze one sample of CNTs (compared to carbon phase analysis) as well as smearing when oxidative atmosphere is used.

FTIR results of thermally annealed CNTs (NC7K ann) are showing, that pristine CNTs (NC7K) are slightly oxidized. As the time and temperature of annealing was rather low, differences in FTIR spectra are sizable. The efficiency can be further enhanced by the increase of time and temperature as well.

Samples treated with nitric acid are showing the biggest grade of oxidation according to FTIR analysis and carbon phase analysis as well, although majority of introduced groups are nitro ones, which does not necessarily mean unsuccessful functionalization, rather the opposite. Nitro groups can be converted to amino groups, making these treatments another possibility for amino-functionalization of CNTs. These treatments also removed ~50% of metallic impurities.

Samples treated with potassium permanganate are showing greatest amount of oxidation with oxidic groups, as presented in FTIR and carbon phase analysis results (samples NC7K F3 and F6). Treatments using solely potassium permanganate were also successful in introduction of carboxylic groups onto CNTs surface. Strong influence of heating during procedure can be observed as well, reducing time required from one day to one hour to achieve similar results. However, residual manganese dioxide is present in these samples, lowering thermal stability of CNTs; thus additional treatment is required to remove it (possibly using HCl). On the contrary, potassium permanganate in combination with sulfuric acid shows low amount of oxidation whilst not leaving manganese dioxide as impurity. This treatment also caused highest damage to CNTs.

Treatment using combination of hydrogen peroxide and sulfuric acid (NC7K F5) can be considered the most successful purification in terms of removal metallic impurities. The removal efficiency is about 85%. Carbon phase analysis also shows the least damage done to CNTs and mediocre oxidation, although carboxylic groups were introduced.

Sample NC7K F7 (treatment using sodium hypochlorite) is probably the least efficient one. It was unsuccessful in removing metal impurities, oxidation grade is mediocre and thermal stability of CNTs is lowered.

Treatment applied on sample NC7Kp was originally aimed to remove amorphous carbon while keeping the oxidation grade low. From obtained results it can be said, that the goal was accomplished.

When it comes to suggest optimal methodology, one must first define demands on final product. From the results can be concluded, that none of the methodologies used are perfect. In most applications, removal of metallic impurities is requested. This can be accomplished quite successfully using mixture of hydrogen peroxide and sulfuric acid. If higher grade of oxidation is required, treatments using nitric acid or potassium permanganate can be subsequently chosen. Nitric acid treatments are more suitable for subsequent amination, while potassium permanganate treatments are more suitable for carboxylation of CNTs (subsequent HCl treatment required).

In case of demand for complex purification, one might suggest utilizing hydrogen peroxide and sulfuric acid treatment followed by HCl treatment to remove metallic impurities and keeping oxidation grade low. Next step would be thermal annealing to remove oxidic groups present, thus graphitizing CNTs.

4 Conclusion

This diploma thesis was focused on covalent functionalization of commercially available industrial grade CNTs (Nanocyl® NC7000). A variety of oxidizers were used for the experimental functionalization of CNTs, different in their oxidation strength, concentration and thermal conditions. All samples were analyzed by SEM, TEM (pristine NC7000 only), Raman spectroscopy, FTIR and carbon phase analysis. Examples of IR spectra were also modeled (by using oxidized SWCNT model).

Functionalization efficiency in terms of damaging CNTs, grade of oxidation, metallic impurities removal and functional groups identification was performed according to results obtained. TEM images were used to measure diameter of nanotubes and number of walls. SEM images were taken to assess morphology of each sample. EDS provided information about elemental composition of metallic impurities. Raman spectroscopy was used to analyze structural integrity; however it turned out to be less efficient to assess changes induced by applied treatments. FTIR analysis provided qualitative information about functional groups presented. Carbon phase analysis was used to measure amount of carbon, hydrogen and metallic impurities in each sample.

Thermal annealing was utilized to assess oxidation grade of pristine CNTs, showing low amount of hydroxylic groups presented in the sample (according to FTIR analysis). It was shown, that the effect of thermal annealing at lower temperatures and intervals can be observed in IR spectra.

Treatments using nitric acid showed high oxidation efficiency and intermediate impurity removal. Majority of the functional groups introduced are probably nitro groups, but it was not confirmed. Functionalization methods utilizing potassium permanganate showed high oxidation efficiency as well. Moreover, these treatments were able to introduced carboxylic groups as well; however they also require subsequent impurity removal treatments.

In terms of metallic impurity removal, the most efficient mixture was the one consisting of hydrogen peroxide. Although oxidation grade was low, removal efficiency was about 85%, making this mixture suitable for purification of CNTs. The overall performance of sodium hypochlorite was weak, probably due to concentration and time of the treatment itself.

From the results it can also be concluded, that efficiencies of treatments used are relative with respect to pristine CNTs provided. Nowadays, there are many manufacturers in the world and the overall quality and composition of their respective products is different, thus making these results not entirely applicable to every CNT product.

5 References

[1] IIJIMA, Sumio. *Helical microtubules of graphitic carbon* [online]. 1991. ISBN 0028-0836. doi:10.1038/354056a0

[2] HUSSAIN, S. Spectroscopic Investigation of Modified Single Wall Carbon Nanotube (SWCNT). *Journal of Modern Physics* [online]. 2011, vol. 02, no. 06, pp. 538–543. ISSN 2153-1196. doi:10.4236/jmp.2011.26063

[3] TAN, Soon Huat, Youngjin CHO, Wonmok LEE, Naesung LEE and Sung Chul HONG. Effect of Cutting and Functionalization of Single-Walled Carbon Nanotubes on Their Dispersion Behaviors. *Journal of Nanoscience and Nanotechnology* [online]. 2011, vol. 11, no. 4, pp. 3350–3357. ISSN 15334880. doi:10.1166/jnn.2011.3721

[4] DUTKO, Ondřej. *Organic molecules interactions with nanostructured carbon*. Ostrava, Czech Republic, 2013. Vysoká škola báňská - Technická univerzita Ostrava. Univerzitní studijní programy

[5] WEPASNICK, Kevin a., Billy a. SMITH, Kaitlin E. SCHROTE, Hannah K. WILSON, Stephen R. DIEGELMANN and D. Howard FAIRBROTHER. Surface and structural characterization of multi-walled carbon nanotubes following different oxidative treatments. *Carbon* [online]. 2011, vol. 49, no. 1, pp. 24–36. ISSN 00086223. doi:10.1016/j.carbon.2010.08.034

[6] HUANG, Jia, Allen L NG, Yanmei PIAO, Chien-Fu CHEN, Alexander a GREEN, Chuan-Fu SUN, Mark C HERSAM, Cheng S LEE and YuHuang WANG. Covalently functionalized double-walled carbon nanotubes combine high sensitivity and selectivity in the electrical detection of small molecules. *Journal of the American Chemical Society* [online]. 2013, vol. 135, no. 6, pp. 2306–12. ISSN 1520-5126. doi:10.1021/ja310844u

[7] KUZMANY, H., a. KUKOVECZ, F. SIMON, M. HOLZWEBER, Ch. KRAMBERGER and T. PICHLER. Functionalization of carbon nanotubes. *Synthetic Metals* [online]. 2004, vol. 141, no. 1-2, pp. 113–122. ISSN 03796779. doi:10.1016/j.synthmet.2003.08.018

[8] SAIFUDDIN, N., a. Z. RAZIAH and a. R. JUNIZAH. Carbon Nanotubes: A Review on Structure and Their Interaction with Proteins. *Journal of Chemistry* [online]. 2013, vol. 2013, pp. 1–18. ISSN 2090-9063. doi:10.1155/2013/676815

[9] SHEN, Cai, Alexandra H BROZENA and YuHuang WANG. Double-walled carbon nanotubes: challenges and opportunities. *Nanoscale* [online]. 2011, vol. 3, no. 2, pp. 503–18. ISSN 2040-3372. doi:10.1039/c0nr00620c

[10] ELLIOTT, James a., Jan K W SANDLER, Alan H. WINDLE, Robert J. YOUNG and Milo S P SHAFFER. Collapse of single-wall carbon nanotubes is diameter dependent. *Physical Review Letters* [online]. 2004, vol. 92, no. 9, pp. 92–95. ISSN 00319007. doi:10.1103/PhysRevLett.92.095501

[11] PARK, Eun-Soo. *Physical and Chemical Properties of Carbon Nanotubes* [online]. 2013. ISBN 978-953-51-1002-6. doi:10.5772/46029

[12] VAN, Lier G, Alsenoy C VAN, Doren V VAN and P GEERLINGS. Ab initio study of the elastic properties of single-walled carbon nanotubes and graphene. *Chem. Phys. Lett.* [online]. 2000, vol. 326, no. Copyright (C) 2012 American Chemical Society (ACS). All Rights Reserved., pp. 181–185. ISSN 00092614. doi:10.1016/s0009-2614(00)00764-8

[13] TETIK, Erkan, Faruk KARADAĞ, Muharrem KARAASLAN and İbrahim ÇÖMEZ. *The Electronic Properties of the Graphene and Carbon Nanotubes: Ab Initio Density Functional Theory Investigation* [online]. 2012. doi:10.5402/2012/416417

[14] RAFIEE, Roham and Reza Maleki MOGHADAM. On the modeling of carbon nanotubes: A critical review. *Composites Part B: Engineering* [online]. 2014, vol. 56, pp. 435–449. ISSN 13598368. doi:10.1016/j.compositesb.2013.08.037

[15] PORRO, S., S. MUSSO, M. VINANTE, L. VANZETTI, M. ANDERLE, F. TROTTA and A. TAGLIAFERRO. Purification of carbon nanotubes grown by thermal CVD. *Physica E: Low-dimensional Systems and Nanostructures* [online]. 2007, vol. 37, no. 1-2, pp. 58–61. ISSN 13869477. doi:10.1016/j.physe.2006.07.014

[16] MAGREZ, Arnaud, Jin Won SEO, Rita SMAJDA, Marijana MIONIĆ and László FORRÓ. Catalytic CVD Synthesis of Carbon Nanotubes: Towards High Yield and Low Temperature Growth. *Materials* [online]. 2010, vol. 3, no. 11, pp. 4871–4891. ISSN 1996-1944. doi:10.3390/ma3114871

[17] SU, Yanjie and Yafei ZHANG. Carbon nanomaterials synthesized by arc discharge hot plasma. *Carbon* [online]. 2015, vol. 83, pp. 90–99. ISSN 00086223. doi:10.1016/j.carbon.2014.11.023

[18] PRASEK, Jan, Jana DRBOHLAVOVA, Jana CHOMOUCKA, Jaromir HUBALEK, Ondrej JASEK, Vojtech ADAM and Rene KIZEK. Methods for carbon nanotubes synthesis—review. *Journal of Materials Chemistry* [online]. 2011, vol. 21, no. 40, p. 15872. ISSN 0959-9428. doi:10.1039/c1jm12254a

[19] RÜMMELI, Mark Hermann, Alicja BACHMATIUK, Felix BÖRRNERT, Franziska SCHÄFFEL, Imad IBRAHIM, Krzysztof CENDROWSKI, Grazyna SIMHA-MARTYNKOVA, Daniela PLACHÁ, Ewa BOROWIAK-PALEN, Gianaurelio CUNIBERTI and Bernd BÜCHNER. Synthesis of carbon nanotubes with and without catalyst particles. *Nanoscale research letters* [online]. 2011, vol. 6, no. 1, p. 303. ISSN 1556-276X. doi:10.1186/1556-276X-6-303

[20] KIM, Kyoung Ju, Woong-Ryeol YU, Ji Ho YOUK and Jinyong LEE. Factors governing the growth mode of carbon nanotubes on carbon-based substrates. *Physical chemistry chemical physics : PCCP* [online]. 2012, vol. 14, no. 40, pp. 14041–8. ISSN 1463-9084. doi:10.1039/c2cp42566a

[21] FENG, Xiaofeng, See Wee CHEE, Renu SHARMA, Kai LIU, Xu XIE, Qunqing LI, Shoushan FAN and Kaili JIANG. In Situ TEM observation of the gasification and growth of carbon nanotubes using iron catalysts. *Nano Research* [online]. 2011, vol. 4, no. 8, pp. 767–779. ISSN 19980124. doi:10.1007/s12274-011-0133-x

[22] SCHÖNFELDER, R., F. AVILÉS, A. BACHMATIUK, J. V. CAUICH-RODRIGUEZ, M. KNUPFER, B. BÜCHNER and M. H. RÜMMELI. On the merits of Raman spectroscopy and thermogravimetric analysis to asses carbon nanotube structural modifications. *Applied Physics A: Materials Science and Processing* [online]. 2012, vol. 106, pp. 843–852. ISSN 09478396. doi:10.1007/s00339-012-6787-8

[23] VAJTAI, Robert. *Springer Handbook of Nanomaterials* [online]. 2013. ISBN 9783642205941. doi:10.1007/978-3-642-20595-8

[24] DRESSELHAUS, M.S., G. DRESSELHAUS, R. SAITO and A. JORIO. Raman spectroscopy of carbon nanotubes. *Physics Reports* [online]. 2005, vol. 409, no. 2, pp. 47–99. ISSN 03701573. doi:10.1016/j.physrep.2004.10.006

[25] HODKIEWICZ, Joe. *Characterizing Carbon Materials with Raman Spectroscopy* [online]. 2010 [accessed. 10. May 2015]. http://www.thermoscientific.com/content/dam/tfs/ATG/CAD/CAD Documents/Application & Technical Notes/Molecular Spectroscopy/Raman/Raman Instruments/D19504~.pdf

[26] ZHAO, Zhiyuan, Zhanhong YANG, Youwang HU, Jianping LI and Xinming FAN. Multiple functionalization of multi-walled carbon nanotubes with carboxyl and amino groups. *Applied Surface Science* [online]. 2013, vol. 276, pp. 476–481. ISSN 01694332. doi:10.1016/j.apsusc.2013.03.119

[27] SYDLIK, Stefanie a., Jae-Hwang LEE, Joseph J. WALISH, Edwin L. THOMAS and Timothy M. SWAGER. Epoxy functionalized multi-walled carbon nanotubes for improved adhesives. *Carbon* [online]. 2013, vol. 59, pp. 109–120. ISSN 00086223. doi:10.1016/j.carbon.2013.02.061

[28] CHIZARI, Kambiz, Alexander VENA, Lars LAURENTIUS and Uttandaraman SUNDARARAJ. The effect of temperature on the morphology and chemical surface properties of nitrogen-doped carbon nanotubes. *Carbon* [online]. 2014, vol. 68, pp. 369–379. ISSN 00086223. doi:10.1016/j.carbon.2013.11.013

[29] ANGELIKOPOULOS, Panagiotis and Henry BOCK. The science of dispersing carbon nanotubes with surfactants. *Physical chemistry chemical physics : PCCP* [online]. 2012, vol. 14, no. 27, pp. 9546–57. ISSN 1463-9084. doi:10.1039/c2cp23436j

[30] MA, Peng Cheng, Naveed A. SIDDIQUI, Gad MAROM and Jang K. KIM. Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: A review. *Composites Part A: Applied Science and Manufacturing*. 2010, vol. 41, no. 10, pp. 1345–1367.

[31] ZHENG, Ming, Anand JAGOTA, Ellen D SEMKE, Bruce A DINER, Robert S MCLEAN, Steve R LUSTIG, Raymond E RICHARDSON and Nancy G TASSI. DNA-assisted dispersion and separation of carbon nanotubes. *Nature materials* [online]. 2003, vol. 2, no. 5, pp. 338–342. ISSN 14761122. doi:10.1038/nmat877

[32] TU, Xiaomin and Ming ZHENG. *A DNA-based approach to the carbon nanotube sorting problem* [online]. 2008. ISBN 1998-0124. doi:10.1007/s12274-008-8022-7

[33] STRONG, Karla L, David P ANDERSON, Khalid LAFDI and John N KUHN. Purification process for single-wall carbon nanotubes. *Carbon* [online]. 2003, vol. 41, no. 8, pp. 1477–1488. ISSN 00086223. doi:10.1016/S0008-6223(03)00014-9

[34] SOULIÉ-ZIAKOVIC, Corinne, Renaud NICOLAŸ, Alexandre PREVOTEAU and Ludwik LEIBLER. Dispersible carbon nanotubes. *Chemistry (Weinheim an der Bergstrasse, Germany)* [online]. 2014, vol. 20, no. 5, pp. 1210–7. ISSN 1521-3765. doi:10.1002/chem.201303818

[35] ERNST, Friederike, Timm HEEK, Antonio SETARO, Rainer HAAG and Stephanie REICH. Functional Surfactants for Carbon Nanotubes: Effects of Design. *The Journal of Physical Chemistry C* [online]. 2013, vol. 117, no. 2, pp. 1157–1162. ISSN 1932-7447. doi:10.1021/jp3098186

[36] WEI, Yan, Zhong-Gang LIU, Xin-Yao YU, Lun WANG, Jin-Huai LIU and Xing-Jiu HUANG. O2-plasma oxidized multi-walled carbon nanotubes for Cd(II) and Pb(II) detection: Evidence of adsorption capacity for electrochemical sensing. *Electrochemistry Communications* [online]. 2011, vol. 13, no. 12, pp. 1506–1509. ISSN 13882481. doi:10.1016/j.elecom.2011.10.004

[37] HOU, Peng-Xiang, Chang LIU and Hui-Ming CHENG. Purification of carbon nanotubes. *Carbon* [online]. 2008, vol. 46, no. 15, pp. 2003–2025. ISSN 00086223. doi:10.1016/j.carbon.2008.09.009

[38] BORTOLAMIOL, Tifania, Petar LUKANOV, Anne-Marie GALIBERT, Brigitte SOULA, Pierre LONCHAMBON, Lucien DATAS and Emmanuel FLAHAUT. Double-walled carbon nanotubes: Quantitative purification assessment, balance between purification and degradation and solution filling as an evidence of opening. *Carbon* [online]. 2014, vol. 78, pp. 79–90. ISSN 00086223. doi:10.1016/j.carbon.2014.06.051

[39] OVEJERO, G, J L SOTELO, M D ROMERO, A. RODRÍGUEZ, M. A. OCAÑA, G. RODRÍGUEZ and J. GARCÍA. Multiwalled Carbon Nanotubes for Liquid-Phase Oxidation. Functionalization, Characterization, and Catalytic Activity. *Industrial & Engineering Chemistry Research* [online]. 2006, vol. 45, no. 7, pp. 2206–2212. ISSN 0888-5885. doi:10.1021/ie051079p

[40] ZHOU, Weiwei, Shun SASAKI and Akira KAWASAKI. Effective control of nanodefects in multiwalled carbon nanotubes by acid treatment. *Carbon* [online]. 2014, vol. 78, pp. 121–129. ISSN 00086223. doi:10.1016/j.carbon.2014.06.055

[41] ROSCA, Iosif Daniel, Fumio WATARI, Motohiro UO and Tsukasa AKASAKA. Oxidation of multiwalled carbon nanotubes by nitric acid. *Carbon* [online]. 2005, vol. 43, no. 15, pp. 3124–3131. ISSN 00086223. doi:10.1016/j.carbon.2005.06.019

[42] TCHOUL, Maxim N, Warren T FORD, Giulio LOLLI, Daniel E RESASCO and Sivaram AREPALLI. Effect of Mild Nitric Acid Oxidation on Dispersability, Size, and Structure of Single-Walled Carbon Nanotubes. *Chemistry of Materials* [online]. 2007, vol. 19, no. 23, pp. 5765–5772. ISSN 0897-4756. doi:10.1021/cm071758l

[43] STOBINSKI, L., B. LESIAK, L. KÖVÉR, J. TÓTH, S. BINIAK, G. TRYKOWSKI and J. JUDEK. Multiwall carbon nanotubes purification and oxidation by nitric acid studied by the FTIR and electron spectroscopy methods. *Journal of Alloys and Compounds* [online]. 2010, vol. 501, no. 1, pp. 77–84. ISSN 09258388. doi:10.1016/j.jallcom.2010.04.032

[44] KIM, Un Jeong, Clascidia A. FURTADO, Xiaoming LIU, Gugang CHEN and Peter C. EKLUND. Raman and IR spectroscopy of chemically processed single-walled carbon nanotubes. *Journal of the American Chemical Society*. 2005, vol. 127, no. 44, pp. 15437–15445.

[45] ROZUMOVÁ, Lucie;, Marianna HUNDÁKOVÁ and Gražyna Simha MARTYNKOVÁ. Methods of purification of carbon nanotubes. *Journal of nanocomposites and nanoceramics*. 2012, vol. 3, no. 1, pp. 21–27. ISSN 0976-6294.

[46] MACKENZIE, Kieran, Oscar DUNENS and Andrew T. HARRIS. A review of carbon nanotube purification by microwave assisted acid digestion. *Separation and Purification Technology* [online]. 2009, vol. 66, no. 2, pp. 209–222. ISSN 13835866. doi:10.1016/j.seppur.2009.01.017

[47] HUANG, Weijie, Yi LIN, Shelby TAYLOR, Jay GAILLARD, Apparao M. RAO and Ya-Ping SUN. Sonication-Assisted Functionalization and Solubilization of Carbon Nanotubes. *Nano Letters* [online]. 2002, vol. 2, no. 3, pp. 231–234. ISSN 1530-6984. doi:10.1021/nl010083x

[48] YANG, De-Quan, Jean-Francois ROCHETTE and Edward SACHER. Functionalization of multiwalled carbon nanotubes by mild aqueous sonication. *The journal of physical chemistry. B* [online]. 2005, vol. 109, no. 16, pp. 7788–94. ISSN 1520-6106. doi:10.1021/jp045147h

[49] KHAMIS, S. M., R. a. JONES, a. T C JOHNSON, G. PRETI, J. KWAK and A. GELPERIN. DNA-decorated carbon nanotube-based FETs as ultrasensitive chemical sensors: Discrimination of homologues, structural isomers, and optical isomers. *AIP Advances* [online]. 2012, vol. 2, no. 2. ISSN 21583226. doi:10.1063/1.4705394

[50] DANIEL, Sobhi, Talasila Prasada RAO, Kota Sreenivasa RAO, Sikhakolli Usha RANI, G.R.K. NAIDU, Hea-Yeon LEE and Tomoji KAWAI. A review of DNA functionalized/grafted carbon nanotubes and their characterization. *Sensors and Actuators B: Chemical* [online]. 2007, vol. 122, no. 2, pp. 672–682. ISSN 09254005. doi:10.1016/j.snb.2006.06.014

[51] RAMANATHAN, T., F. T. FISHER, R. S. RUOFF and L. C. BRINSON. Amino-fimctionalized carbon nanotubes for binding to polymers and biological systems. *Chemistry of Materials* [online]. 2005, vol. 17, no. 8, pp. 1290–1295. ISSN 08974756. doi:10.1021/cm048357f

[52] SHELIMOV, Konstantin B, Rinat O ESENALIEV, Andrew G RINZLER, Chad B HUFFMAN and Richard E SMALLEY. Purification of single-wall carbon nanotubes by ultrasonically assisted filtration. *Chemical Physics Letters* [online]. 1998, vol. 282, no. 5-6, pp. 429–434. ISSN 00092614. doi:10.1016/S0009-2614(97)01265-7

[53] SHAO, Lidong, Gerard TOBIAS, Christoph G SALZMANN, Belén BALLESTEROS, Sung You HONG, Alison CROSSLEY, Benjamin G DAVIS and Malcolm L H GREEN. Removal of amorphous carbon for the efficient sidewall functionalisation of single-walled carbon nanotubes. *Chemical communications (Cambridge, England)* [online]. 2007, vol. 1, no. 47, pp. 5090–2. ISSN 1359-7345. doi:10.1039/b712614j

[54] PARK, Young Soo, Young Chul CHOI, Keun Soo KIM, Dong-Chul CHUNG, Dong Jae BAE, Kay Hyeok AN, Seong Chu LIM, Xiao Yan ZHU and Young Hee LEE. High yield purification of multiwalled carbon nanotubes by selective oxidation during thermal annealing. *Carbon* [online]. 2001, vol. 39, no. 5, pp. 655–661. ISSN 00086223. doi:10.1016/S0008-6223(00)00152-4

[55] FABBRO, Chiara and Tatiana DA ROS. Local 'repristinization' of oxidized single-walled carbon nanotubes by laser treatment. *Carbon* [online]. 2014, vol. 76, pp. 96–104. ISSN 00086223. doi:10.1016/j.carbon.2014.04.054

[56] KONDRATYUK, Petro and John T YATES. Molecular views of physical adsorption inside and outside of single-wall carbon nanotubes. *Accounts of chemical research* [online]. 2007, vol. 40, no. 10, pp. 995–1004. ISSN 0001-4842. doi:10.1021/ar700013c

[57] PAN, Bo and Baoshan XING. Adsorption Mechanisms of Organic Chemicals on Carbon Nanotubes. *Environmental Science & Technology* [online]. 2008, vol. 42, no. 24, pp. 9005–9013. ISSN 0013-936X. doi:10.1021/es801777n

[58] LIKODIMOS, Vlassis, Theodore a. STERIOTIS, Sergios K. PAPAGEORGIOU, George Em. ROMANOS, Rita R.N. MARQUES, Raquel P. ROCHA, Joaquim L. FARIA, Manuel F.R. PEREIRA, José L. FIGUEIREDO, Adrián M.T. SILVA and Polycarpos FALARAS. Controlled surface functionalization of multiwall carbon nanotubes by HNO3 hydrothermal oxidation. *Carbon* [online]. 2014, vol. 69, pp. 311–326. ISSN 00086223. doi:10.1016/j.carbon.2013.12.030

[59] AVILÉS, F., J.V. CAUICH-RODRÍGUEZ, L. MOO-TAH, A. MAY-PAT and R. VARGAS-CORONADO. Evaluation of mild acid oxidation treatments for MWCNT functionalization. *Carbon* [online]. 2009, vol. 47, no. 13, pp. 2970–2975. ISSN 00086223. doi:10.1016/j.carbon.2009.06.044

[60] ZHANG, Jin, Hongling ZOU, Quan QING, Yanlian YANG, Qingwen LI, Zhongfan LIU, Xinyong GUO and Zuliang DU. Effect of Chemical Oxidation on the Structure of Single-Walled Carbon Nanotubes. *The Journal of Physical Chemistry B* [online]. 2003, vol. 107, no. 16, pp. 3712–3718. ISSN 1520-6106. doi:10.1021/jp027500u

[61] WANG, Li, Shouai FENG, Jianghong ZHAO, Jianfeng ZHENG, Zhijian WANG, Li LI and Zhenping ZHU. A facile method to modify carbon nanotubes with nitro/amino groups. *Applied Surface Science* [online]. 2010, vol. 256, no. 20, pp. 6060–6064. ISSN 01694332. doi:10.1016/j.apsusc.2010.03.120

[62] ROCHA, Raquel P., Adrián M.T. SILVA, Saudi M.M. ROMERO, Manuel F.R. PEREIRA and José L. FIGUEIREDO. The role of O- and S-containing surface groups on carbon nanotubes for the elimination of organic pollutants by catalytic wet air oxidation. *Applied Catalysis B: Environmental* [online]. 2014, vol. 147, pp. 314–321. ISSN 09263373. doi:10.1016/j.apcatb.2013.09.009

[63] KIM, Sang Won, Taehoon KIM, Yern Seung KIM, Hong Soo CHOI, Hyeong Jun LIM, Seung Jae YANG and Chong Rae PARK. Surface modifications for the effective dispersion of carbon nanotubes in solvents and polymers. *Carbon* [online]. 2012, vol. 50, no. 1, pp. 3–33. ISSN 00086223. doi:10.1016/j.carbon.2011.08.011

[64] SITKO, Rafal, Beata ZAWISZA and Ewa MALICKA. Modification of carbon nanotubes for preconcentration, separation and determination of trace-metal ions. *TrAC Trends in Analytical Chemistry* [online]. 2012, vol. 37, pp. 22–31. ISSN 01659936. doi:10.1016/j.trac.2012.03.016

[65] TASIS, Dimitrios, Nikos TAGMATARCHIS, Vasilios GEORGAKILAS and Maurizio PRATO. Soluble carbon nanotubes. *Chemistry (Weinheim an der Bergstrasse, Germany)* [online]. 2003, vol. 9, no. 17, pp. 4000–8. ISSN 0947-6539. doi:10.1002/chem.200304800

[66] WANG, Ronghui, Sara TOMBELLI, Maria MINUNNI, Maria Michela SPIRITI and Marco MASCINI. Immobilisation of DNA probes for the development of SPR-based sensing. *Biosensors and Bioelectronics* [online]. 2004, vol. 20, no. 5, pp. 967–974. ISSN 09565663. doi:10.1016/j.bios.2004.06.013

[67] CHEN, Changlun, Bo LIANG, Di LU, Akihisa OGINO, Xiangke WANG and Masaaki NAGATSU. Amino group introduction onto multiwall carbon nanotubes by NH3/Ar plasma treatment. *Carbon* [online]. 2010, vol. 48, no. 4, pp. 939–948. ISSN 00086223. doi:10.1016/j.carbon.2009.10.033

[68] ASSALI, Mohyeddin, Manuel Pernía LEAL, Inmaculada FERNÁNDEZ, Pablo ROMERO-GOMEZ, Rachid BAATI and Noureddine KHIAR. Improved non-covalent biofunctionalization of multi-walled carbon nanotubes using carbohydrate amphiphiles with a butterfly-like polyaromatic tail. *Nano Research* [online]. 2010, vol. 3, no. 11, pp. 764–778. ISSN 19980000. doi:10.1007/s12274-010-0044-2

[69] UDDIN, Nasir M., Franco M. CAPALDI and Bakhtier FAROUK. Molecular dynamics simulations of carbon nanotube dispersions in water: Effects of nanotube length, diameter, chirality and surfactant structures. *Computational Materials Science* [online]. 2012, vol. 53, no. 1, pp. 133–144. ISSN 09270256. doi:10.1016/j.commatsci.2011.07.041

[70] SUNG, Sae Jin, Taehoon KIM, Seung Jae YANG, Jun Young OH and Chong Rae PARK. New insights into the oxidation of single-walled carbon nanotubes for the fabrication of transparent conductive films. *Carbon* [online]. 2015, vol. 81, pp. 525–534. ISSN 00086223. doi:10.1016/j.carbon.2014.09.085

[71] RASTOGI, Richa, Rahul KAUSHAL, S K TRIPATHI, Amit L SHARMA, Inderpreet KAUR and Lalit M BHARADWAJ. Comparative study of carbon nanotube dispersion using surfactants. *Journal of colloid and interface science* [online]. 2008, vol. 328, no. 2, pp. 421–8. ISSN 1095-7103. doi:10.1016/j.jcis.2008.09.015

[72] ZAMINPAYMA, Esmaeil and Kavoos MIRABBASZADEH. Interaction between single-walled carbon nanotubes and polymers: A molecular dynamics simulation study with reactive force field. *Computational Materials Science* [online]. 2012, vol. 58, pp. 7–11. ISSN 09270256. doi:10.1016/j.commatsci.2012.01.023

[73] NANOCYL. *NANOCYL NC7000 series - Product Datasheet – Thin Multi-Wall Carbon Nanotubes* [online]. May 2009. Available at: http://www.nanocyl.com

[74] CHOVANEC, Ondřej. *Využití uhlíkatých nanotrubiček pro odstranění ibuprofenu a diklofenaku z vod*. Ostrava, Czech Republic, 2015. Vysoká škola báňská - Technická univerzita Ostrava.

[75] XIA, Hui, Yu WANG, Jianyi LIN and Li LU. Hydrothermal synthesis of MnO2/CNT nanocomposite with a CNT core/porous MnO2 sheath hierarchy architecture for supercapacitors. *Nanoscale Research Letters* [online]. 2012, vol. 7, no. 1, p. 33. ISSN 1556-276X. doi:10.1186/1556-276X-7-33

[76] SOCRATES, G. *Infrared and Raman characteristic group frequencies* [online]. 2001. ISBN 978-0-470-09307-8. doi:10.1002/jrs.1238

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